

# From Water to H<sub>2</sub>O: Using the Human Dimension of Science To Teach the Nature of Science

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**ABSTRACT:** The long and complex history to define the composition of water as H<sub>2</sub>O is summarized. This case study could be useful not only to introduce the history of chemistry in the classroom but also to teach the basic tenets of the nature of science (NOS). Water has been present in several turning points in the history of chemistry such as the first steps of pneumatic chemistry, the chemical revolution, the beginning of the atomic theory, early electrochemistry, and the theory of ionic dissociation. The human dimension of science has been chosen as one of the numerous possibilities offered by the water case study to teach NOS. For this purpose, topics involved in the history of water such as Van Helmont's "tree experiment", the "water controversy", the revival of Avogadro's hypothesis by Cannizaro, some scientific highlights of Arrhenius and Laurent, and the identification of oxygen are analyzed.

**KEYWORDS:** *History/Philosophy, Water/Water Chemistry, High School/Introductory Chemistry, Inquiry-Based/Discovery Learning, Public Understanding/Outreach*

## INTRODUCTION

The use of a historical approach to understanding science dates back to the 1950s when the *Harvard Case Histories in Experimental Science* were edited by Conant<sup>1</sup> and adapted for teaching in high schools by Klopfer.<sup>2</sup> Nowadays, historical cases together with student inquiry and contemporary cases are widely accepted approaches to teaching the nature of science (NOS).<sup>3</sup>

Allchin et al. analyze merits and deficits of these three modes of NOS instruction concluding the value of history for "contextualizing NOS lessons, especially on theory change and the cultural (including biographical) contexts of science, and other aspects that embody long time scales and expansive human contexts".<sup>4</sup> "Difficult or time-consuming for teachers to learn background or historical perspective" is concluded as one of the deficits. Wandersee and Griffard define as a formidable challenge to "distillate" a complex history of events in such a way that it is still accurate, and suitable for use in teaching.<sup>5</sup>

Several projects, such as "The Story Behind the Science", "The Minnesota Case Study Collection", and HIPST profiled by Clough,<sup>6</sup> Allchin,<sup>7</sup> and Höttecke et al.,<sup>8</sup> respectively, aim to help teachers to overcome that deficit. None of these projects considers the long and complex history to establish the composition of water as H<sub>2</sub>O.

This case study is especially useful to introduce the history of chemistry in the classroom since it includes several turning points in the history of chemistry such as the first steps of the pneumatic chemistry, the chemical revolution, beginning of the atomic theory, early electrochemistry, and theory of ionic dissociation. Additionally, it can serve as a good starting point for the knowledge of essential chemists such as Boyle, Priestley, Cavendish, Lavoisier, Dalton, Berzelius, and Arrhenius among others. It could also help to introduce the scientific method or Kuhn's general theory of scientific revolutions with, for example, the help of the "tree experiment"

of Van Helmont or the downfall of the Berzelius electrochemical paradigm, respectively. It could fully illustrate that knowledge is a continuous struggle to overcome prejudice, authoritarianism, and even "common sense" as expressed by Postman when advocating an historical approach to teaching.<sup>9</sup>

Once focused on the nature of science, it can be used to explain and reflect on its five basic tenets considered appropriate for primary to secondary school learning and summarized by Waikato University.<sup>10</sup> In fact, the history of water is an excellent example of the "tentative and empirical nature of scientific knowledge, of the subjective interpretation that different scientists can make of the same empirical observations, of the inferential, imaginative and creative nature of science, and, finally, of the influence that social, cultural and scientific community can have in the scientific knowledge".

In the first part of this article, the complex history of the composition of water is distilled from Partington,<sup>11–13</sup> Leicester,<sup>14</sup> Brock,<sup>15</sup> and Chang.<sup>16</sup> In its second part, the human dimension of science has been chosen as one of the numerous possibilities offered by the water case study to teach NOS. For this purpose, topics such as Van Helmont's "tree experiment", the "water controversy", the revival of Avogadro's hypothesis by Cannizaro, some scientific highlights of Arrhenius and Laurent, and the identification of oxygen are analyzed. They show the existence of scientific biases, the need of a proper exchange of information in the scientific community, the progress of science by building on previous knowledge, the success and frustrations in conducting research, and, finally the power of human curiosity, creativity, and imagination as driving force for the development of science.

**Received:** January 28, 2018

**Revised:** August 24, 2018

**Published:** September 18, 2018

Table 1. Relevant Scientists and Their Contributions to the History of Understanding Water

Year	Scientist	Contribution
1650	Van Helmont (1579–1644)	“Tree experiment” published in 1648 ( <i>Ortus Medicinæ</i> ): Water as a primary element
	Boyle (1627–1691)	<i>The Sceptical Chymist</i> (1661): Doubt about the elementary nature of water
1700	Stahl (1660–1674)	<i>Specimen Beccherianum</i> (1703): Phlogiston as the principle of fire
	Hales (1677–1761)	<i>Vegetable Staticks</i> (1727): Beginning of pneumatic chemistry
1750	Black (1728–1799)	<i>Experiments upon Magnesia Alba, Quicklime, and Some Other Alkaline Substances</i> (1756): A gas can take part in chemical reactions (be “fixed”)
	Priestley (1733–1804)	<i>Decomposition of Mercuric Oxide</i> (1774): Discovery of oxygen (“dephlogisticated air”)
	Lavoisier (1743–1794)	Report to the Royal Academy of Sciences (December 1783): Correct components of water
	Cavendish (1731–1810)	<i>Experiments on Air</i> (1784): Phlogistonist interpretation of the combustion of hydrogen (“inflammable air”)
	Nicholson (1753–1815) and Carlisle (1768–1840)	Decomposition of water by electricity (1800); Early electrochemistry
1800	Dalton (1766–1844)	“Rule of greatest simplicity” (1803); Chemical combination only between different types of atoms; Beginning of atomic theory
	Avogadro (1776–1856)	<i>Essai d’une Manière de Déterminer les Masses Relatives des Molécules Élémentaires des Corps...</i> (1811); Hypothesis of diatomic molecules for hydrogen and oxygen as components of water against Dalton and Berzelius theories
	Berzelius (1779–1848)	Third volume of his <i>Lärbok</i> (1818): Electrochemical dualistic system; Chemical combinations are the result of electrical attraction between atoms of opposite electric charges
	Dumas (1800–1884)	Synthesis of trichloroacetic acid by the action of chlorine on acetic acid (1839); Downfall of Berzelius’s electrochemical theory
	Williamson (1824–1904)	Investigation on the “etherification” process (1850); Oxygen has the ability to hold together two atoms or groups of atoms
1850	Cannizaro (1826–1910)	Revival of Avogadro’s hypothesis at Karlsruhe Congress (1860): $2\text{H}_2 + \text{O}_2 \rightarrow 2\text{H}_2\text{O}$
	Arrhenius (1859–1927)	<i>On the Dissociation of Substances Dissolved in Water</i> (1887); Some molecules of water are dissociated into electrical charged ions; Theory of ionic dissociation

Contents related to the history of chemistry, such as the historical development of atomic models, the contributions of scientists like Lavoisier and Avogadro, and the evolution of the acid–base theories, are already present in the Spanish Curriculum for Secondary Education. The water case study can help teachers to explain those topics from a different perspective, and it allows a new possibility for the introduction of the history of chemistry in the curriculum.

The final target of this article is to stimulate students’ interest in the history of chemistry by enjoying the puzzle that arises with the gradual knowledge of water’s composition.

A timeline of the major contributions involved in the historical evolution of the concept of water from element to compound is shown in Table 1.

## ■ SUMMARY OF THE HISTORY OF WATER

### In the Beginning: Water as a Primary Element

And God said, “Let the waters under the sky be gathered together into one place, and let the dry land appear.” And it was so.

This quotation from *Genesis* is one of the examples of the importance of water in the ancient cultures. Unlike its first day creation, the Babylonians regarded water as the first uncreated principle. Furthermore, Persians worshipped water together with earth, fire, and wind, and the Egyptians had the water goddess Anuket as a personification of the Nile, the lifeblood of the ancient Egypt.

The earlier greek philosophers considered that the material world consisted of one or other of the 4 “elements”: fire, air, water, and earth. Thereby, Thales (624–546 B.C.) postulated that water was the primary substance from which everything was made, and Herakleitos (540–480 B.C.) seemed to admit only 3 of them: fire, water, and earth. Empedokles’ (492–432 B.C.) contribution was to take into account all 4 elements, which, when mixed together in various proportions, generated perceptible substances. His “theory of the 4 elements” was to

remain the fundamental basis of theoretical chemistry until 18th century.

Aristotle (384–322 B.C.) developed this theory introducing the idea of the possible transmutation of water into earth with a long tradition in the history of chemistry. In fact, in 1746 Johann Eller still argued that water could be changed into both earth and air by the action of fire or phlogiston, and even Lavoisier spent time designing an experiment on the distillation of water to confirm his suspicion that the “earth” described in Eller’s experiment was really derived from the glass of the apparatus by a leaching effect.

Joan Baptista Van Helmont (Brussels, 1579–1644) was strongly anti-Aristotelian and rejected the 4 elements theory, asserting that the true elements were air and water, with air being purely a physical medium, which did not participate in transmutations. He sought to prove it with his famous “tree experiment” in which a willow branch, implanted into dried earth and watered daily for 5 years, became a tree. After drying and reweighing the earth he found that its mass was almost unchanged (“wanting about 2 ounces”), hence erroneously concluding that the tree arose out of only water.

The “skeptical chemist” Robert Boyle (Waterford, Ireland, 1627, to London, 1691) did not agree with the theory of the 4 elements and argued against the experiment of the burning wood used at that time as a typical defense of that theory: i.e., fire, air (smoke), water (bubbling from the ends of the logs), and earth (ash) as results of the combustion. However, Boyle was no advocate of Helmont’s water theory since, for example, he could not find an explanation for the formation of metals or minerals from water. Moreover, he did not support the elementary nature of water, and he doubted that water could be converted into earth.

### Water toward H<sub>2</sub>O: Pneumatic Chemistry

The development of pneumatic chemistry (the chemistry of “air”) in the 18th century played a fundamental role in the long way from water to H<sub>2</sub>O. The assumption of the alchemists that the gases, “spiritus”, evolved during their experiments were just

air together with the difficulty of handling them prevented any progress in the determination of their nature.

Van Helmont, who devised the name of “gas”, was the first to recognize that gases different from air existed; among others the “spiritus sylvestris” (carbon dioxide) formed during the burning of charcoal. However, he did not investigate further, because, as he wrote: “The gases cannot be contained in a vessel, as they break out through all impediments and unite with the surrounding air”.<sup>17</sup>

The answer to Van Helmont’s concern about a suitable apparatus to collect gases had to wait for almost one century with Stephen Hales (Bekesbourne, Kent, 1677, to Teddington, near London, 1761) in his “Vegetable Staticks” published in 1727. He constructed the earliest form of a gas-collection apparatus in which the gas generator was separated from the receiver unlike previous designs in which gases had been evolved and collected in the same vessel.

In spite of Van Helmont’s opinion, and the success of Hales in isolating many gases, the general view in the first half of the 18th century was that all gases were composed of air. One of the reasons for the interest and very fast growth of pneumatic chemistry in the second half of that century was the classical series of experiments that Joseph Black (Bordeaux, 1728, to Edinburgh, 1799) published in 1756 (*Experiments upon Magnesia Alba, Quicklime, and Some Other Alkaline Substances*, 1756). Black’s conclusions about “fixed air” (carbon dioxide) encouraged Joseph Priestley (Fieldhead, near Leeds, 1733, to Northumberland, Pennsylvania, 1804) and Henry Cavendish (Nice, 1731, to London, 1810) among others, to develop Hales’ apparatus to study different varieties of air, “factitious airs”.

Although Carl Wilhelm Scheele (Stralsund, 1742, to Köping, 1786) had already isolated what he called “fire air” in the years 1771–2, Priestley, unaware of the Scheele’s studies, was the first to report the discovery of oxygen (“dephlogisticated air”) derived from his famous experiment on the decomposition of mercuric oxide made in 1774.

The generation of “air” by the action of acids on iron had been already described by Boyle in 1660. However, Cavendish is generally regarded as the discoverer of “inflammable air” (hydrogen) due to the systematic study of this gas, published in 1766. Cavendish concluded erroneously that hydrogen came from the metals, and he considered that the inflammable air was the phlogiston contained in the metals.

### Water Still an Element under the Phlogiston Theory

The origin of the phlogiston theory can be traced back to Johann Joachim Becher (Speyer, 1635, to London?, 1682?) and one of his three earthy principles: the terra pinguis (fatty earth) that was subsequently developed by Georg Ernst Stahl (Anspach, Bavaria, 1660, to Berlin, 1734) under the name of phlogiston, from the Greek word for burned or inflammable. Phlogiston was released from all flammable substances during their combustion and could be transferred from one substance to another. That characteristic could explain chemical reactions such as the recovery of metals from their metallic oxides (metals deprived of phlogiston) by heating them with a phlogiston-rich substance like charcoal, or the interconversion of sulfur and sulfuric acid that was one of the founding experiments of the phlogiston chemistry carried out by Stahl.

The phlogiston theory was the first attempt to explain different chemical phenomena from a unified point of view. By mid-18th century, it was the dominant theory of chemistry.

The most respected European chemists interpreted their results on the basis of the phlogiston theory using a “phlogistonist language” with terms such as “dephlogisticated air” (oxygen) mentioned in this section.

The pioneering studies on electricity in the second half of the 18th century and the progress of pneumatic chemistry came together in the evolution of the concept of water from element to compound. In fact, Priestley and Cavendish, together with John Warltire (Wolverhampton, 1738, to Tamworth, 1810), performed experiments based on firing mixtures of inflammable air with common air or dephlogisticated air in closed vessels by an electric spark.

Before 1781, Priestley was the first to observe that the inside of the glass vessel became dewy when carrying out that type of experiment. Warltire’s interpretation of this phenomenon was that “common air deposits its moisture when it is phlogisticated”.<sup>12</sup>

In his “Experiments on Air” published in 1784, Cavendish quantified the qualitative observations of Priestley and Warltire. In the case of the combustion of inflammable air with common air, he stated that “by this experiment 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” (*Philosophical Transactions of the Royal Society*, 1784, lxxiv, 141, cited by Partington),<sup>12</sup> whereas for the combustion with dephlogisticated air he concluded that the ratio of the combining volumes of the two gases was 2.02.

The expected conclusion would have been that when inflammable air (hydrogen) and dephlogisticated air (oxygen) are mixed in proper proportions they produce water which, consequently, is a compound of those 2 substances. In fact, Cavendish was the first to discover this experimental fact. However, he gave a phlogistonist interpretation to their results. Oxygen was water deprived of its phlogiston (water – phlogiston), and hydrogen was phlogisticated water (water + phlogiston). Therefore, water was a component of both gases, and it was produced when the excess and deficit of phlogiston canceled out; (water – phlogiston) + (water + phlogiston) = water. This explanation allowed the phlogistonists to continue with the ancient idea that water was an element.

### Water Is Widely Accepted as a Compound: Chemical Revolution

James Watt (Greenock, Scotland, 1736, to Heathfield, near Birmingham, 1819) is usually acknowledged as the first one to consider water as a compound but without reaching a true knowledge of the components. In April 1783, he considered water to be formed from dephlogisticated air and “phlogiston” by using a different interpretation than the one given by Cavendish to the combustion of hydrogen. For Watt, phlogiston could mean hydrogen but also any kind of inflammable air, including carbon monoxide.

A few months later, in December 1783, Antoine Laurent Lavoisier (Paris, 1743–1794) was the first to publish the correct components of water as “the oxygen principle with the inflammable aqueous principle”, concluded from the same type of experiments already carried out by Priestley, Warltire, Cavendish, and Watt. This time, the inflammable aqueous principle unambiguously meant hydrogen since it was obtained from iron or zinc and dilute sulfuric acid.

Additionally, Lavoisier and Jean Baptiste Meusnier (Tours, 1754, to Mainz, 1793) made a demonstration of the decomposition of water by passing through the red hot iron

tube of a gun barrel a current of steam or by dropping it in water. They showed that inflammable air was produced while the iron in the gun barrel was oxidized.

### Electrolysis of Water: A Puzzle To Be Solved

In 1800, a few years after Lavoisier's death, the use of the pile designed by Volta allowed William Nicholson (London, 1753–1815) and Anthony Carlisle (Stillington, Durham, 1768, to London, 1840) to find a new method to decompose water. This experiment, which seemed to be the decisive confirmation of the compound nature of water, revealed the so-called “distance problem”: If water is decomposed by the action of electricity, why do the oxygen and hydrogen gases emerge at two different and distant points corresponding to the electrodes?

Johann Wilhelm Ritter (Samnitz, Silesia, 1776, to Munich, 1810) explained that phenomenon coming back to the view of water as an element. The electrolysis (term introduced later by Faraday) of water was not a decomposition but a pair of syntheses: of oxygen by the combination of water with positive electricity and of hydrogen by the combination of water with negative electricity. Therefore, the two gases evolved at separate electrodes corresponding to the supply of the two types of electricity. This hypothesis, that could avoid the “distance problem”, agreed with Cavendish's earlier idea that hydrogen was phlogisticated water by identifying phlogiston with negative electricity. Ritter's synthesis view of electrolysis attracted the attention of those who opposed Lavoisier's new system of chemistry.

In the beginning of the 19th century, different theories were proposed by the advocates of compound water to solve the distance problem but without being completely convincing. One of them, the “molecular chains” hypothesis, gained a wide following with Christian Johann von Grotthuss (Leipzig, 1785, to Gedutz, Livonia, 1822) as its main author. In 1806, he viewed the Voltaic pile as “an electrical magnet”, and assumed that the water molecules would line up into a chain like a set of little bar magnets, alternating positive hydrogen and negative oxygen particles, between the poles of the Voltaic pile. Therefore, the electrical polarity in the water molecules was induced by the battery. The release of oxygen and hydrogen would be explained by the electrical repulsion/attraction from the poles. In his initial model, Grotthuss considered water as being composed of one atom of oxygen and another one of hydrogen. Shortly after, he gave an updated model in which he assumed water was HO<sub>2</sub>.

In 1833, Michael Faraday (Newington, Surrey, 1791, to Hampton Court, Surrey, 1867), who was intrigued by the “distance problem”, reviewed and criticized earlier theories of electrolysis in his work “on electrochemical decompositions”. He stated that “electrochemical decomposition does not depend upon any direct attraction and repulsion of the poles” against Grotthuss' idea. Accordingly, he, with the help of William Whewell (Lancaster, 1794, to Cambridge, 1866), introduced a new nomenclature including the term “electrodes” which were not poles of attraction. Faraday erroneously concluded that all electrolytes must contain 1 equiv of each of the elements into which they are decomposed; hence, water was HO.

### Composition of Water by Early Electrochemical and Atomic Theories

The atomic theory of John Dalton (Eaglesfield, 1766, to Manchester, 1844) arrived around the same time as that the

early electrochemistry. In 1803, Dalton stated in his notebook the “rule of greatest simplicity”; i.e. if only 1 compound of 2 kinds of atoms A and B is known, it is, unless there is some reason to the contrary, A + B. Therefore, water would be composed of 1 atom of oxygen and 1 of hydrogen (HO). As an additional argument to reject the possibility of H<sub>2</sub>O for water, Dalton considered that chemical combination could only happen between different types of atoms with enough chemical affinity. The impossibility of the combination between atoms of hydrogen had also been established by, at that time, the emerging electrochemical dualistic system of Humphry Davy (Penzance, 1778, to Geneva, 1829) and Jöns Jacob Berzelius (Väversunda, 1779, to Stockholm, 1848), based on the hypothesis that chemical combinations are the result of the electrical attraction between atoms of opposite electrical charges. The foundation of this theory was that atoms contain different amounts of the two opposite electricities, thus a net electrical charge exists. From this basis, Berzelius elaborated an electrochemical series of elements from the most electro-negative, oxygen, to the most electropositive, potassium, with chlorine being highly electronegative as mentioned in the next section.

Amedeo Avogadro (Turin, 1776–1856) concluded the H<sub>2</sub>O formulation by taking into account that “the relative number of molecules in a compound is given at once by the ratio of the volumes of the gases that form it” as stated in his publication of 1811 (*Essai d'une manière de déterminer les masses relatives des molécules élémentaires des corps et les proportions selon lesquelles elles entrent dans ces combinaisons, Journal de Physique*, 1811, lxxiii, 58–76, cited by Partington).<sup>13</sup> He explained the experimental fact that 2 volumes of water are formed with a 2 to 1 combination of hydrogen and oxygen by assuming double atom molecules for both (2H<sub>2</sub> + O<sub>2</sub> → 2H<sub>2</sub>O). Avogadro's ideas were rejected by Dalton and most other chemists and forgotten for 50 years until their revival by Stanislao Cannizzaro (Palermo, 1826, to Rome, 1910), and therefore, much of early electrochemistry and atomic theory forged ahead on the assumption that water was HO without a definite explanation of the distance problem. Moreover, the literal meaning of the term electrolysis, coined by Faraday in 1833, was completely accepted by that time, and consequently, substances prone to electrolysis, such as water or potash, were concluded to be compounds giving up definitely the view of water as an element.

### The End: Water = H<sub>2</sub>O and Solution to the “Distance Problem”

The final stage of the history “from water to H<sub>2</sub>O” started in the 1830s with the research project of Jean Baptiste Dumas (Alais, 1800, to Cannes, 1884) on the hydrogen–chlorine substitution. The substitution of the electropositive hydrogen by the highly electronegative chlorine was not possible for the then-dominant Berzelius' electrochemical dualistic theory. In fact, Dumas was careful to avoid the term substitution in the beginning. By 1839, after his successful synthesis of trichloroacetic acid by the action of chlorine on acetic acid, Dumas was convinced of the one-by-one direct atomic replacement of hydrogen by chlorine, and he finally came out against Berzelius electrochemical theory. This conclusion opened the door to the possibility of diatomic molecules of like-charged atoms in order to explain the synthesis of water, as previously suggested by Avogadro.

The very similar properties of trichloroacetic and acetic acids were the origin of the so-called “type theory” developed by Dumas in his work published in 1840, “On the Law of Substitutions and the Theory of Types”. By 1856, Charles Gerhardt (Strasbourg, 1816–1856) had suggested 4 types, water, ammonia, hydrogen, and hydrochloric acid, regarding a “type” as a constitutional template defining a set of related substances in terms of properties and chemical reactions. In the case of the “water type”, Gerhardt was building on the previous works of Auguste Laurent (La Folie, near Langres, 1808, to Paris, 1853) and Alexander Williamson (London, 1824, to Hindhead, Surrey, 1904).

Laurent foreshadowed the idea of the water type in his article of 1846 when he suggested that alcohol, ether, and potassium hydroxide could be represented or classified as substitution products of water: OHH, OEtH, OEtEt, OHK, respectively. This idea was experimentally confirmed in 1850 by Williamson in his investigation on the “etherification” process. He concluded that ether ( $C_4H_{10}O$ ) was “a coupled compound containing two ethyl groups,  $C_2H_5$ , and not merely the oxide of a single radical,  $C_4H_{10}$ ” and, therefore, ether could be represented as water ( $H_2O$ ) in which both atoms of hydrogen had been replaced by the ethyl radical,  $C_2H_5$ .<sup>16</sup> The extension of his investigation to asymmetric ethers confirmed that conclusion and showed that oxygen had the ability to hold together two atoms or groups of atoms in the “water type” compounds.

The idea that an oxygen atom really did bind two hydrogen atoms in water was consolidated by the introduction of the concept of valency in the mid 1850s. In this way, there was a general agreement that water was  $H_2O$  by the 1860s. However, the so-called “distance problem” continued without a definite explanation.

The final answer to the “distance problem” came in 1850 when Williamson suggested that in any chemical system a molecule is continually exchanging atoms or radicals with other molecules: “in a drop of hydrochloric acid, hydrogen and chlorine atoms of different molecules continually exchange partners, and during the process they must exist for a very small time in the free state” (*Philosophical Magazine*, 1850, xxxvii, 350, cited by Partington).<sup>13</sup> In the mid-1850s, Rudolf Clausius (Köslin, Poland, 1822, to Bonn, 1888) agreed with Williamson hypothesis and considered the possibility of some free atoms of hydrogen and oxygen present in water as well as all other possible combinations of H and O ( $HO$ ,  $H_2O$ ,  $HO_2$ ,  $H_2O_2$ ,  $H_nO_m$ ) that could join and also spontaneously dissociate with a definite probability. He also proposed the responsibility of the products coming from the spontaneous dissociation for conducting the electrical current.

The Williamson–Clausius hypothesis was considered by Svante Arrhenius (Vik, near Uppsala, 1859, to Stockholm, 1927) in his thesis of 1884 anticipating his theory of ionic dissociation which was definitely stated in his article “On the dissociation of substances dissolved in water” (*Zeitschrift für physikalische Chemie*, I, 631, 1887). According to this theory, some molecules of water are already dissociated into electrically charged ions:  $H^+$  and  $OH^-$ , before any electrical current is applied. These pre-existing ions finally solved the “distance problem” that arose at the beginning of the 19th century.

## ■ HUMAN DIMENSION OF SCIENCE IN THE WATER CASE STUDY

### “Tree Experiment” of Van Helmont: A Biased Approach of Data

The “willow tree experiment” of Van Helmont is usually regarded as the first known quantitative experiment in biology. He introduced in a pot 200 pounds of earth, previously dried in a furnace, and implanted a 5 pound stem of a willow. After 5 years watering the plant, he found, what he considered, the same 200 pounds of earth, although “wanting about 2 ounces”. From this quantitative result, Van Helmont erroneously concluded that “164 pounds of wood, barks, and roots arose out of water onely” (*Ortus Medicinæ*, 1648, cited by Partington).<sup>11</sup>

His biased approach to data was based on his belief in water as the primary element from which all other matter is derived. Following the arguments of Hershey, that approach prevented Van Helmont from considering additional experiments and looking for alternative interpretations that would have contributed to a faster growth of the scientific knowledge at that time.<sup>18</sup>

First of all, Van Helmont ignored his own experimental result of 2 ounces of earth lost during the experiment, assuming that it could be either blown away by the wind or carried away by the water. Second, he claimed that 164 pounds of willow resulted from only water, although he did not measure the amount of water added to the plant during the 5 years.

Finally, Van Helmont recognized the existence of a gas, different from air, that was released when burning oak charcoal, and he called it “spiritus sylvester” (carbon dioxide). However, his full conviction that water was the only reason for the growth of the tree made him disregard the possible role of carbon dioxide, and therefore, a great opportunity for significant progress in plant biology was lost.

### “Water Controversy”: The Need for a Proper Exchange of Information in the Scientific Community

The lack of reference of previous works, due to deliberate action, ignorance, unavailability, or poor scientific communication, is detected in the so-called “Water Controversy”. This term concerns the claims of Cavendish, Watt, and Lavoisier to have been the discoverers of the composition of water, and it has been thoroughly analyzed by Partington.<sup>12</sup> As Blagden, Cavendish’s assistant, wrote in a letter published in 1786, and cited by Partington: “In the spring of 1783, Mr Cavendish communicated to me and other members of the Royal Society the result of some experiments... He showed us that, from them, water was dephlogisticated air united to phlogiston. About the same time the news was brought to London that Mr Watt of Birmingham had been induced by some experiments to hold a similar view. Soon after this I went to Paris, and in the company of Mr Lavoisier and some other members of the Royal Academy of Sciences I gave some account of these experiments”.<sup>12</sup> From this letter, a poor scientific communication from Cavendish and Watt, “personal communication” or “news” respectively, could be derived.

Blagden’s information was so impressive for Lavoisier that, almost immediately, in June 1783, he, together with Laplace (Beaumont, 1749, to Paris, 1827), carried out an experiment of burning hydrogen. In December 1783, before the publication of the “Experiments on Air” of Cavendish, Lavoisier published the results and the correct composition

of water without proper acknowledgment, at least in the opinion of the advocates of Cavendish, of the previous work and ideas of Cavendish about the synthesis of water.

### Revival of Avogadro's Hypothesis by Cannizzaro: Science as a Collective Enterprise, Building on Previous Knowledge

The history of the evolution of the concept of water from element to compound is a good example of the contribution of scientists from different areas to the construction of scientific knowledge, and the progress of science by building on previous existing knowledge. For example, the information given to him by Priestley, about oxygen, and by Blagden, about the Cavendish and Watt experiments on the combustion of hydrogen, played a fundamental role in Lavoisier being the first to publish the correct components of water in December 1783.

Sometimes the answer is already in the bibliography but ignored for years until a favorable context arises and somebody seeks out and supports it. This could be the case of the revival of Avogadro's ideas about water by Cannizzaro described in more detail by Williams.<sup>19</sup>

For his hypothesis, Avogadro paid attention to the theory from Joseph Louis Gay-Lussac (Saint-Léonard-de-Noblat, 1778, to Paris, 1850) about the simple ratios of volume followed by gases in their chemical combinations. In 1784, Cavendish had already concluded a 2:1 ratio between the volumes of hydrogen and oxygen combining to make water; therefore,  $\text{H}_2\text{O}$  was a reasonable formulation for water coming from  $2\text{H} + \text{O} \rightarrow \text{H}_2\text{O}$ . However, the experimental result showed that two volumes of water vapor are formed instead of the expected one. To explain this fact, Avogadro assumed diatomic molecules of oxygen and hydrogen:  $2\text{H}_2 + \text{O}_2 \rightarrow 2\text{H}_2\text{O}$ . This explanation was against the widely accepted, at that time, theories of Dalton and Berzelius. In the atomic theory of Dalton, atoms contained self-repellent caloric, and chemical combination could only happen if the attractive force of chemical affinity between different types of atoms was enough to overcome the self-repulsion of caloric. For the electrochemical dualism of Berzelius, two atoms of the same kind have the same electric charge, so they would repel each other.

When Cannizzaro presented Avogadro's ideas in the Karlsruhe Congress in 1860, the Berzelius theory had already been dismissed, and the Williamson investigation on the "etherification" process had showed that oxygen had the ability to hold together two atoms or groups of atoms. Therefore, now the scientific community was ready to accept what 50 years before it had ignored.

### Arrhenius and Laurent: Success and Frustrations in Conducting Research

Let us imagine the mood of Arrhenius after his conversation with Cleve, his professor of chemistry, in the initial phase of his research work, cited by Chang: "I said, 'I have a new theory of electrical conductivity as a cause of chemical reactions.' He said, 'This is very interesting,' and then he said 'Goodbye.' He explained to me later that he knew very well that there are so many different theories formed, and that they are almost all certain to be wrong, for after a short time they disappeared; and therefore by using the statistical manner of forming his ideas, he concluded that my theory would not exist long".<sup>16</sup>

Despite that discouraging comment, Arrhenius presented his doctoral thesis, based on the conductivities of electrolytes, at

the University of Uppsala in 1884. A new disappointment came when his dissertation was only awarded a fourth class which normally excluded him from university teaching in Uppsala.

Arrhenius did not give up and sent copies of his thesis to Europe's leading electrochemists, including Ostwald who was impressed and offered him a post in Riga. Finally, and with the threat of Ostwald's offer, Arrhenius was appointed docent in Uppsala and obtained a traveling scholarship that enabled him to work not only with Ostwald but also with Kohlrausch, Boltzmann, and van't Hoff. In 1887, he articulated his full theory of ionic dissociation in his work "On the dissociation of substances dissolved in water", and his brilliant scientific career was crowned with the Nobel Prize in Chemistry in 1903.

Sometimes researchers are not honored during their life; on the contrary, their theories have the opposition of reputed scientists. In despite of all the difficulties and frustrations, they are able to defend their ideas, and finally, after their death, they are recognized for their contribution to the progress of science. This was the case of Laurent.

When Laurent began to work as Dumas' assistant in 1831, the radical theory, derived from the electrochemical theory of Berzelius, was firmly established. In his "Essai sur la théorie des proportions chimiques" of 1819, Berzelius applied dualistic principles to organic compounds asserting that they consisted of electronegative oxygen combined with an electropositive compound radical; in other words, organic compounds had the general composition  $(\text{XYZ})^+\text{O}^-$ , where X, Y, and Z are C, H, and N. The term "radical" referred, at that time, to a group of atoms that reacted as a unit retaining its identity through a series of reactions.

In 1834, Dumas published his results about the formation of chloral and chloroform by the action of chlorine on alcohol. A year later, Dumas introduced the term substitution for the replacement of one portion of hydrogen by one portion of chlorine observed in the formation of chloral.

Around the same time, Laurent isolated naphthalene from coal tar and studied its halogen derivatives. In 1835, he concluded a stepwise replacement of portions of hydrogen by equivalent portions of halogen in the different chlorinated and brominated products synthesized.

Dumas vacillated, but Laurent did not hesitate in interpreting those reactions as evidence of the substitution of electropositive hydrogen by electronegative chlorine, which was electrochemically "impossible".

This outraged Berzelius, who, in 1838, regretted that Dumas "has advocated the idea that a chlorine atom can replace a hydrogen atom" which "is contrary to the first-principles of chemistry".<sup>13</sup> On the other hand, his comment "Laurent's rare talent for research is greatly diminished in value by his complicated and bizarre views" shows his antagonism against Laurent.

Dumas also attacked Laurent in his answer to Berzelius' criticism: "The law of substitution is an empirical fact and nothing more... I am not responsible for the gross exaggeration with which Laurent has invested my theory; his analyses moreover do not merit my confidence".<sup>13</sup>

The hostility of the most prominent chemists of his time, such as Berzelius, Dumas, or even Liebig, had unfavorable results for Laurent. For much of his professional life, Laurent was exiled to Bordeaux, and in 1850, he competed unsuccessfully for the vacant Chair of Chemistry at the College de France. Bitterly disappointed, his health declined

due to the tuberculosis contracted in his unhealthy laboratory, and he finally died in 1853 at the early age of 44.

In 1838, his hostility toward Laurent did not prevent Dumas from following Laurent's interpretation for his experiments on the chlorination of acetic acid and the properties of the resulting trichloroacetic acid. One year later, Dumas definitely rejected the Berzelius dualistic view, and a "unitary theory" began gradually to be accepted. In the new theory, the molecule as a whole was regarded as a structure which could generate related molecules, by modification of its parts.

Despite all the difficulties, Laurent was not the only protagonist in the downfall of Berzelius' dualistic theory, but he also significantly contributed to the structural theory of organic molecules and foreshadowed new ideas as the "water type" subsequently developed by Gerhardt.

### Identification of One of Water's Components: Oxygen. The Power of Human Curiosity, Imagination, and Creativity

Our inquisitive nature is probably the most intrinsically human driving force for the development of science. Curiosity, together with imagination and creativity, was also involved in the progressive understanding of the nature of water as it is already shown in this work. For years, numerous and prestigious scientists were puzzled with the identification of the components of water, and their related phenomena, such as calcination in which the action of oxygen remained unknown for centuries. Observation and subsequent curiosity were present in questions such as the following: Why do metals increase their weight when calcined? Imagination and creativity were needed in its answer.

Boyle's curiosity on the increase in weight of metals on calcination, already known by the metallurgists of the Middle Ages, led him to carry out experiments on the calcination of tin, published in 1673 (*New Experiments to make Fire and Flame Stable and Ponderable*, cited by Partington).<sup>11</sup> He observed an increase of weight in the open air as well as in an assumed air-free sealed retort, interpreting that fire particles penetrated the glass and were absorbed by the metal. Almost one century later (1756), Mikhail Lomonosov (Kholmogory, 1711, to St. Petersburg, 1765) demonstrated that the weight of a metal remains unchanged after it is heated in a sealed retort if it is completely free of air. In that time interval, the belief in the fire particles lost ground and the phlogiston introduced by Stahl became the dominant theory in chemistry.

Stahl assumed that all flammable compounds contained phlogiston, which was released into the air during combustion. He considered that air was essential for combustion but just as a mere receptacle for the phlogiston emitted by the burning bodies. The phlogiston theory readily explained the known facts of combustion of organic compounds in which the final products weighed less than the initial substances due to the loss of phlogiston.

However, the explanation of the increase in weight of metals on calcination had to wait until the mid-18th century, starting with Black's curiosity about phenomena such as the loss in weight when magnesia alba was calcined, and the formation of a crust on exposing limewater to air. "Fixed air" (carbon dioxide) was Black's answer in both cases. In his experiments, Black demonstrated that a gas could take part in chemical reactions (be "fixed"), and also that although "fixed air" was present in air, it was a different gas, against the existing idea about the elementary nature of air.

Black's results increased the curiosity of chemists for the study of gases. One of them was Priestley, whose contribution was essential to answer why metals increase their weight on calcination. In 1774, he was greatly puzzled by the "air" evolved when mercuric oxide decomposed directly into mercury without the addition of charcoal, when subjected to very high temperatures by means of a burning glass lens. He described it as a new gas "five or six times better than common air, for the purpose of respiration, inflammation, and, I believe, every other use of common atmospherical air" (Letter of 15 March 1775 to James Pringle, the President of the Royal Society of London, cited by Chang),<sup>16</sup> and, following a phlogistonist interpretation, named it "dephlogisticated air" (oxygen) since the new air was so pure that it was free from phlogiston.

This surprising result immediately attracted the attention of Lavoisier who had been intrigued for years about how air was absorbed and released by solid compounds when burned. Scientific curiosity was finally satisfied with Lavoisier's answer in 1778: "The principle which unites with metals during calcination, which increases their weight and which is a constituent part of the calx is nothing else than the healthiest and purest part of air, which after entering into combination with a metal, (can be) set free again" (*Histoire de l'Académie Royale des Sciences*, revised *Mémoire*, 1778, cited by Brock).<sup>15</sup>

## CONCLUSIONS

This article shows the usefulness of the "history of water" as a case study approach to introduce the history of chemistry in high school education. Essential episodes, as well as relevant figures of the history of chemistry, can be introduced in the classroom by means of the long and complex history to define the composition of water as H<sub>2</sub>O. Moreover, it can be applied to teach some basic tenets of the nature of science (NOS) by the analysis of the human dimension of science involved in this case study.

The existence of scientific biases and the need of a proper exchange of information in the scientific community are illustrated by the "tree experiment" of Van Helmont, and the "water controversy", respectively. Prestigious scientists, such as Avogadro, Cannizzaro, Laurent, and Arrhenius, are considered to reflect about the progress of science by building on previous knowledge, and the success and frustrations in conducting research. Finally, the identification of one of water's components, oxygen, and its action in the calcination of metals is chosen as an example of the power of human curiosity, creativity and imagination as driving force for the development of science.

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### Notes

The authors declare no competing financial interest.

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