



Chemical Education

A CHIMIA Column

Why the Karlsruhe Congress of 1861 had to happen!

Ho Ho Ho! When Water was Diatomic

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Abstract: When he introduced the concept of atomic weights at the beginning of the 19th Century CE, John Dalton assumed that water had the formula HO. This assumption resulted in a half century of confusion – partly because on a scale of H = 1, he defined the atomic weights O = 8 and C = 6, and partly because elements that could exhibit variable valency appeared to possess different atomic (or rather equivalent) weights. The correction of the formula of water, together with the recognition of the diatomic nature of the gases hydrogen and oxygen, were formalized following the Karlsruhe congress of 1861 and allowed the establishment of the ‘modern’ and consistent atomic weights.

Keywords: Atomism · Chemical history · Water

Our modern image of Father Christmas, with his trademark “Ho Ho Ho!” salutation probably stems from Clement Clarke Moore’s 1844 poem *A Visit from St. Nicholas* which describes its eponymous elf thus “He had a broad face and a little round belly, That shook when he laughed, like a bowlful of jelly” (Fig. 1). But to a chemist HO symbolizes a compound composed of one atom each of oxygen and hydrogen.



Fig. 1. The phrase “Ho Ho Ho!” is associated with Father Christmas in Christian tradition (Souvenir Post Card Company, New York – eBayfrontback, Public Domain, <https://commons.wikimedia.org/w/index.php?curid=37488397>).

For much of its life, water was an element, sharing centre-stage with the fellow Aristotelean elements air, earth and fire! This idyllic state came to an end about 1781 CE, when James Watt, Henry Cavendish, Antoine Lavoisier and Jean Baptiste Meusnier independently demonstrated the formation of water from, and the decomposition of water to, hydrogen and oxygen. Over the next ten years, Gaspard Monge, Louis Lefèvre-Gineau, Antoine François

Fourcroy, Louis Nicolas Vauquelin and Armand Seguin confirmed these results and by the turn of the Century, there was a general agreement that the weight ratio of oxygen to hydrogen in water was approximately 7:1 and the volume relationship in the reaction of hydrogen and oxygen gas was 1:2. John Dalton was aware of these studies and summarized them in his 1808 work ‘A New System of Chemical Philosophy’,^[1] which introduced modern atomic theory to the extended chemical community following his first announcement of “the relative weights of the ultimate particles of gaseous and other bodies” in 1803.^[2]

In the 1808 book, Dalton recognized that it was necessary to know “the number of less compound particles (atoms) which enter into the formation of one more compound particle” in order to determine “the relative weights of the ultimate particles”.^[1] He defined a number of rules, of which the first was “When only one combination of two bodies can be obtained, it must be presumed to be a binary one, unless some cause appear to the contrary” (Fig. 2). This assumption, which was logical in the absence of any other basis to determine stoichiometry, became known as “the rule of simplicity” and was to result in a half century of confusion! Dalton applied his first rule to water and as “only one compound of oxygen and hydrogen is certainly known” assigned it the formula HO (or $\odot\odot$ as he denoted it). As Dalton had arbitrarily assigned a relative weight of one to hydrogen, and one mass unit of hydrogen reacted with seven mass units of oxygen, it followed that the relative weight of oxygen was seven. Actually, Dalton did not always adhere rigorously to his own rules, and he commented that “it must be allowed to be possible that water may be a ternary compound. In this case, if two atoms of hydrogen unite to one of oxygen, then an atom of oxygen must weigh 14 times as much as one of hydrogen”.^[1]

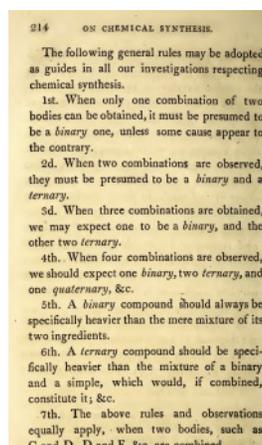


Fig. 2. Dalton’s rules for the formulation of chemical species (from ref. [1], vol. 1, part 1). The assumption of the formula HO for water was to result in 50 years of confusion in the chemical world.

Should Dalton have realised that the combining ratio of hydrogen to oxygen of 2:1 implied that water should be formulated H₂O? Probably not, because it was not until three years later, in 1811, that Amadeo Avogadro, in work that was to be ignored for

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a further 50 years, postulated that equal volumes of gases at the same conditions of temperature and pressure contained the same number of particles.^[3] By 1813, Berzelius had postulated “water to be a compound of 2 atoms of hydrogen and 1 atom of oxygen” (denoted H or H°O) on the basis of the reaction volumes of H_2 and O_2 and following the law of combining volumes discovered by Joseph Louis Gay-Lussac in 1808.^[4,5] Berzelius also proposed a new scale of relative weights with $\text{H} = 6.636$ and $\text{O} = 100$.^[4] For some reason, this was not embraced by the chemical community!

As more accurate measurements were made, the weight of oxygen was adjusted to $\text{O} = 8$ on the $\text{H} = 1$ scale. If we consider the molecule CO , formed from the reaction of 12 mass units of carbon with 16 mass units of oxygen, then the Dalton atomic weight of $\text{O} = 8$ leads to an atomic weight of $\text{C} = 6$. This in turn results in analysis of carbon compounds leading to formulae having twice as many carbon atoms as the present formula. For example, the atomic weight of chlorine (35.5) was known from the reaction of hydrogen with chlorine to give HCl , and the molecular weight of chloroform can be calculated from its vapour density giving a weight of ≈ 120 and a formula of C_2HCl_3 . The problem became exacerbated by some chemists using the scale ($\text{H} = 1$, $\text{C} = 6$, $\text{O} = 8$), others ($\text{H} = 1$, $\text{C} = 6$, $\text{O} = 16$) and yet others ($\text{H} = 1$, $\text{C} = 12$, $\text{O} = 16$).

By the middle of the 19th Century CE, the result was chaos and a trend emerged to use ‘equivalent weights’ rather than Dalton’s atomic weights. The equivalent weight is the quantity of a substance that reacts with a fixed quantity of another substance. Organic acids were typically characterized as their silver salts: the equivalent weight of acetic acid ($\text{CH}_3\text{CO}_2\text{H}$, molar mass 60) combining with 108 g of silver would be 60, whereas for oxalic acid ($\text{HO}_2\text{CCO}_2\text{H}$, molar mass 90) it would be 45. The difficulties were not only in organic chemistry, but also in inorganic chemistry, where atomic weights were derived from the oxides, which in turn relied on $\text{O} = 8$.

The formation of metal oxides in different valence states further complicated matters and various ingenious theories were developed to rationalize their existence – Kekulé rejected the idea of variable valence and introduced the ‘dot notation’ ($\text{PCl}_5 = \text{PCl}_3 \cdot \text{Cl}_2$), whilst Laurent and Dumas postulated that ‘chemical atoms’ might actually be molecular groups, composed of smaller atoms.

The concept of equivalent weights persisted in the use of normality rather than molarity until recently; titration of a 1M solution of sulfuric acid against 1M sodium hydroxide solution requires twice the volume of NaOH to reach neutrality – the sulfuric acid solution was, thus, described as 2N.

In his 1861 text-book, August Kekulé identified 19 different structural formulae which had been proposed for acetic acid (formulated $\text{C}_2\text{H}_4\text{O}_4$, Fig. 3)!^[6] Kekulé had already rationalized the formulae into a common scheme ($\text{C} = 6$, $\text{O} = 8$, $\text{H} = 1$, $\Theta = 12$, $\Theta = 16$). Clearly, something had to be done! The consequence was the organization of a congress in 1861 at Karlsruhe by August Kekulé, Adolphe Wurtz, and Karl Weltzien. The aims of the congress were to reach an accord on chemical nomenclature, notation, structure and atomic weights, and it is fair to say that this meeting transformed the science of chemistry. One of the most important consequences was that the chemical community became aware of the work of Avogadro, which had been ignored for the previous 50 years. This was almost entirely the result of contributions from Stanislaw Cannizzaro,^[7] together with the distribution of his 1858 publication which showed how the ideas and results of Avogadro, Dumas and Gaudin, amongst others, could be combined to generate a consistent and rational set of atomic weights. This also established the diatomic nature of the gases H_2 and O_2 .

And what of HO ? Today we recognize three species containing a single oxygen and hydrogen atom: HO^- , HO^\bullet and HO^+ . The first of these, HO^- , is the familiar hydroxide ion. The name ‘hydroxide’ was being used for minerals as early as 1824,^[8,9] although the term ‘hydrate’ persisted in the chemical literature. The hydroxide ion

$\text{C}_2\text{H}_4\text{O}_4$	empirische Formel.
$\text{C}_2\text{H}_4\text{O}_4 + \text{HO}$	analitische Formel.
$\text{C}_2\text{H}_4\text{O}_4 + \text{H}$	Wasserstofftheorie.
$\text{C}_2\text{H}_4 + \text{O}_4$	Kernteorie.
$\text{C}_2\text{H}_4\text{O}_4 + \text{HO}_2$	Lowenham's Ansicht.
$\text{C}_2\text{H}_4 + \text{H}_2\text{O}_4$	Ornham's Ansicht.
$\text{C}_2\text{H}_4\text{O}_4 + \text{O} + \text{HO}$	Radicaltheorie.
$\text{C}_2\text{H}_4 + \text{O}_4 + \text{HO}$	Radicaltheorie.
$\text{C}_2\text{H}_4\text{O}_4\text{O}_2$	Gerhardt. Typentheorie.
$\text{C}_2\text{H}_4\text{O}_4$	Typentheorie(Schischkoff)etc.
$\text{C}_2\text{O}_4 + \text{C}_2\text{H}_4 + \text{H}_2\text{O}$	Berzelius' Paarungstheorie.
$\text{H}_2\text{O} \cdot (\text{C}_2\text{H}_4\text{O}_4)_2$	Kulbe's Ansicht.
$\text{H}_2\text{O} \cdot (\text{C}_2\text{H}_4\text{O}_4)_2 + \text{O}_2$	ditto
$\text{C}_2(\text{C}_2\text{H}_4\text{O}_4)_2$	Wurtz.
$\text{C}_2\text{H}_4(\text{C}_2\text{O}_4)_2$	Mendius.
$\text{C}_2\text{H}_4\text{HO}(\text{C}_2\text{O}_4)_2$	Geuther.
C_2O_4	Roehleder.
$\left(\text{C}_2\frac{\text{H}_4}{\text{O}}\right)_2 + \text{HO}$	
$\left(\text{C}_2\frac{\text{H}_4}{\text{CO}} + \text{CO}_2\right) + \text{HO}$	Persoz.
$\text{C}_2\frac{\text{H}_4}{\text{H}}\text{O}_4$	
$\frac{\text{C}_2}{\text{H}}\text{O}_4$	Berth.

Fig. 3. The 19 different formulae for acetic acid which Kekulé represented in his 1861 text book (Public domain, https://commons.wikimedia.org/wiki/File:Kekule_acetic_acid_formulae.png).

is, of course, the species identified by Arrhenius as the ‘base’ in aqueous conditions.^[10]

Less familiar are the species HO^\bullet (hydroxyl or oxidanyl) and HO^+ (hydroxylum or oxidanylium). HO^\bullet is an odd-electron species described as a radical and is one of a number of highly reactive oxygen species (ROS) with significant biological effects, both on pathogens and host organisms. Ironically, the first evidence for the formation of HO^\bullet radicals probably came from a 1924 spectroscopic study of emissions associated with H_2 - O_2 combustion reaction by Eatson, thus, completing the cycle back to the formulation of water as HO by Dalton a century earlier.^[11] In addition to their role as an oxidant in biology, HO^\bullet radicals have a more important function in maintaining the health and equilibrium of our planet. The reaction with methane is one of the major pathways by which the greenhouse gas methane is removed from the atmosphere. The hydroxyl radical is not only a terrestrial species, but has also been detected in the interstellar medium, the first confirmed observation being in 1963.^[12]

Whereas HO^\bullet is a seven valence electron species, the hydroxylum cation is even more electron-deficient and possesses only six valence electrons. This cation has also been observed in the interstellar medium^[13,14] but the first spectroscopic identification appears to date from 1933 when the cation was one of the species formed in the electrodeless discharge of water vapour.^[15]

I hope that the reader has enjoyed this little chemical cycle that started and ended with water and the hydrogen-oxygen reaction. Finally, in the spirit of “Ho, Ho, Ho!”, I offer seasonal greetings to all of the readers of *CHIMIA*.

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