Two Hypotheses of Avogadro (1811)

by Bernard Fernandez, PhD,
Honorary research fellow at the Commissariat à l'Énergie atomique

ABSTRACT

This analysis of a text by Avogadro from 1811 recounts an episode on the long road towards the characterisation of atoms and the ascertainment of their reality. This road saw notable advances between 1790 and 1820, before slowing down until the turn of the 20th century, and the pace was set during this period by the formulation of Dalton's atomic theory (between 1803 and 1806) and by Gay-Lussac 's experimental observations on the volumes of gases (in 1808). Avogadro took the apparently contradictory works of these two chemists as his basis, and reconciled them by venturing two hypotheses. The first, known as Avogadro's hypothesis, lead to the present notion of the mole, and is characterised by the Avogadro number (N). The second allowed for a distinction to be made between O and O_2, namely, the atom and its molecule, and is the basis for the notion of a molecule and present chemical notation.

FOREWORD

Avogadro's text is difficult for today's minds to follow, being as they are totally accustomed to the notion of atoms and molecules: it is convenient to read these terms bearing in mind that the notions were quasi-unknown in 1811. They could only be inferred from some experimental facts, which made them evidently rather distant. Let us also remark that the term 'molecule' is used for what we now call 'atom'.

Furthermore, it is important to signal that Avogadro's text, apart from his luminous hypotheses, contains a certain number of considerations and suppositions that have since been rejected.

AMEDEO AVOGADRO, THE UNKNOWN

Amedeo Avogadro, Count of Quaregna and Ceretto (born in Turin on 9th August 1776, died in the same city on 9th July 1856), is an exceptional figure in the particularly fertile history of physics of the beginning of the 19th century.[1]

Piedmont was part of the Kingdom of Sardinia then, administered in a very autocratic way by king Victor Amadeus III. Due to punctilious censorship numerous scientists emigrated, among them two famous savants: the mathematician Giuseppe Ludovico Lagrangia (1736-1813), known under frenchified name Joseph-Louis Lagrange, and the chemist Claude Louis Berthollet (1748-1822), a medical doctor educated in Turin.

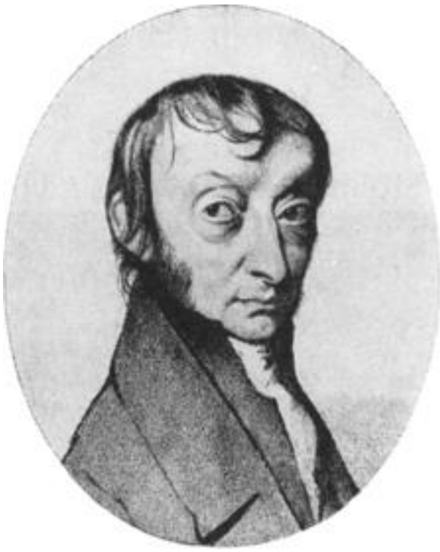


Fig1 : Portrait of Amedeo Avogadro

The issue of an ancient Piedmontese magistrate family, Avogadro at first followed the family route by undertaking studies in law and theology, entering *l'Avvocatura dei Poveri* in 1896, then *l'Avvocatura Generale.* When in 1801 France annexed Piedmont, Avogadro became *Secrétaire du Département* d'Eridanus.[2] From this point he took an interest in natural sciences and mathematics. He attended a university course in physics and read a lot in his free time. In 1804, aged 28, he sent two essays on electricity to the Academy of Sciences of Turin, of which he became a corresponding member. Two years later he addressed two memoirs on electricity, this time in French, to the *Journal*

1. See the well-documented biography by Mario Morselli, *Amedeo Avogadro, A Scientific Biography,* Dordrecht Publishing Co, Dordrecht 1984.
2. *Le département d'Eridanus*, from the Greek name of the Po river, was one of the six French departments that constituted Piedmont.

de Physique, de Chimie, d'Histoire Naturelle et des Arts, a magazine run by Jean-Claude de la Méthérie.[3] In 1809, Avogadro was nominated professor of mathematics and physics at the ancient *Collège Royal* in Vercelli, a town located some 50 kilometres east of Turin. In 1820, he became professor of physics at the University of Turin, a post he held for the rest of his life (with a break from 1823 to 1833, seemingly due to his occupation of political posts). Avogadro led a withdrawn life we know little about. He never sought honours nor travelled beyond Piedmont. Aged 38, he married Felicita Mazzia, with whom he had seven children.

The text in focus here is a memoir submitted to *Journal de Physique*[4] in spring 1811, and published in July of that year. The title, 'Essay on Determining the Relative Masses of the Elementary Molecules of Bodies and the Proportions by Which They Enter These Combinations', announces an ambitious programme. It formulated what is now known as Avogadro's hypothesis.

THE PREMISES : LAVOISIER (1789), PROUST, AND RICHTER (1794)

The end of the 19th century saw a revolution in chemistry. A major player in this was Antoine Laurent Lavoisier (1743-1794), who, thanks to the systematic use of weighing scales ascertained the real nature of combustion and confuted the theory of phlogiston.

The theory of phlogiston, an ancient theory of combustion

In order to explain the combustion of bodies, German chemist Johann Joachim Becher (1635-1682) created the theory of phlogiston, which was further developed by Georg Ernst Stahl (1660-1734). Phlogiston (from the Greek *phlogistos*, meaning flammable) was a fluid contained in all flammable bodies, given off during combustion or oxidation. These bodies were hence being

3. A. Avogadro, 'Considérations sur l'état dans lequel doit se trouver une couche d'un corps non-conducteur de l'électricité, lorsqu'elle est interposée entre deux surfaces douées d'électricités de différente espèce', *Journal de physique, de chimie, d'histoire naturelle et des arts*, Issue 63, p.450-462, December 1806; 'Second mémoire sur l'électricité', *ibid.* 65, p.130-145, August 1807.
4. Amedeo Avogadro, 'Essai de déterminer les masses relatives des molécules élémentaires des corps, et les proportions dans lesquelles elles entrent dans ces combinaisons', *Journal de Physique, de Chimie, d'Histoire naturelle et des arts,* Issue 73, p.58-76, 1811. This article is a part of the book (unfortunately run out) *Les atomes, une anthologie historique*; texts selected, presented and annotated by Bernadette Bensaude-Vincent & Catherine Kounelis, Paris, Presses-Pocket, 1991. One may also consult *Histoire de l'atome, a* collection of texts selected and presented by Pierre Radvanyi, Belin, 2007.

dephlogistated - deprived of phlogiston. However, measurements showed that the mass of metals increases during combustion: but this made some scientists even suppose that phlogiston had negative mass. Lavoisier showed that combustion is a combination of body and oxygen, namely oxidation.

He also showed that air was a mixture of oxygen, nitrogen, etc. Most importantly, he established the notion of a 'simple body' or an 'element' - a non-decomposable chemical substance, as opposed to a 'compound body':

> *We must admit, as elements, all the substances into which we are capable, by any means, to reduce bodies by decomposition. [...] we ought never to suppose them compounded until experiment and observation has proved them to be so.*[5]

In 1794 Joseph-Louis Proust (1754-1826) stated in a general way the law of constant composition as a result of experimental studies on iron oxides and oxides of other metals. His article "Recherches sur le bleu de Prusse"[6] was not published until 1799, though a considerable extract appeared in *Journal de Physique* (1794):[7]

> [...] *these experiments* [prove] *the principle which I established at the beginning of this memoir; namely, that iron is, like several other metals, subject by that law of nature which presides over all true combinations, to two constant proportions of oxygen. It does not at all differ in this regard from tin, mercury, lead etc. and finally from virtually all of the known combustibles…I will make known the kind of oxide that results from the combination of oxygen with carbon, in a lower proportion to that corresponding to carbon dioxide (carbon monoxide).*

What Proust designates as the 'true combination', is what we now call a 'chemical combination', in opposition to 'mixture' (for example table salt, NaCl, is a chemical combination of chlorine and sodium in a fixed proportion, one atom of one substance for one atom of the other. Salt has no physical or chemical property of one or the other. This is different from a simple mixture, without combination, which can be made in whatever proportion). In the same time, German chemist Jeremias Benjamin Richter (1762-1807) also stated this law of

5. Antoine Laurent Lavoisier, *Elements of Chemistry* , Edinburgh, 1790, transl. R. Kerr, Preface, p. xxiv.
6. Joseph-Louis Proust, 'Recherches sur le bleu de Prusse', *Journal de Physique, de Chimie, d'Histoire naturelle et des Arts*, vol.VI, issue 50, p. 241–251, 1799.
7. Joseph-Louis Proust, 'Extrait d'un Mémoire intitulé: Recherches sur le Bleu de Prusse', *Journal de Physique, de Chimie, d'Histoire naturelle et des Arts*, vol.II, issue 45, p. 334–341, November 1794.

constant composition, formulated in a work of three volumes[8] published between 1792 and 1794, in which he introduced the term stoichiometry to designate the way of measuring the relative proportions of elements in a chemical compound. Unfortunately his work, in German and in a style difficult to follow, was little disseminated and remained rare. It was through the relation by Berthollet in his book *Essai de statique chimique,*[9] published in 1803, that Richter became known.

DALTON (1803, 1810): THE FOUNDATIONS OF MODERN ATOMISM

The law of constant composition had an impact on the English physicist John Dalton (1766-1844). For him the sole explanation was that all substances were composed of atoms - elements that combined themselves to form compound bodies. Based on some general hypotheses, he saw there a means to determine the relationships between masses of diverse bodies. In his notebook we may find on 6th September 1803:

> *(i) matter consists of small ultimate particles or atoms*
> *(ii) atoms indivisible and cannot be created or destroyed [...]*
> *(iii) all atoms of a given element are identical and have the same invariable weight*
> *(iv) atoms of different elements have different weights*
> *(v) the particle of a compound is formed from a fixed number of atoms of its fixed of is component elements (law of fixed proportions)* [10]

Dalton uses the term 'particle' for what we now call a 'molecule', the smallest part of a substance. He uses the word 'atom' to refer to the tiniest part of a simple body or an element. His theory is exposed in a book, the first part of which appeared in 1808, the second in 1810 and the last in 1827.[11] In the first part, after having stated the principles, he draws up a list of possible ways in which two or more atoms can combine:

> *If there are two bodies, A and B, which are disposed to combine the following is the order in which the combinations may take place beginning with the most simple, namely:*
> *1 atom of A + 1 atom of B = 1 atom of C, binary,*

8 Jeremias Benjamin Richter, *Anfangsgründe der Stöchyometrie oder Meßkunst chymischer Elemente,* (3 vols.) J. F. Korn, Breslau & Hirschberg, 1792-94.

9 Claude-Louis Berthollet, *Essai de statique chimique,* Firmin Didot, Paris, 1803.

10 Quote from James Riddick Partington, *A History of Chemistry,* London, MacMillan, 1931-1964; vol. III, p. 784.

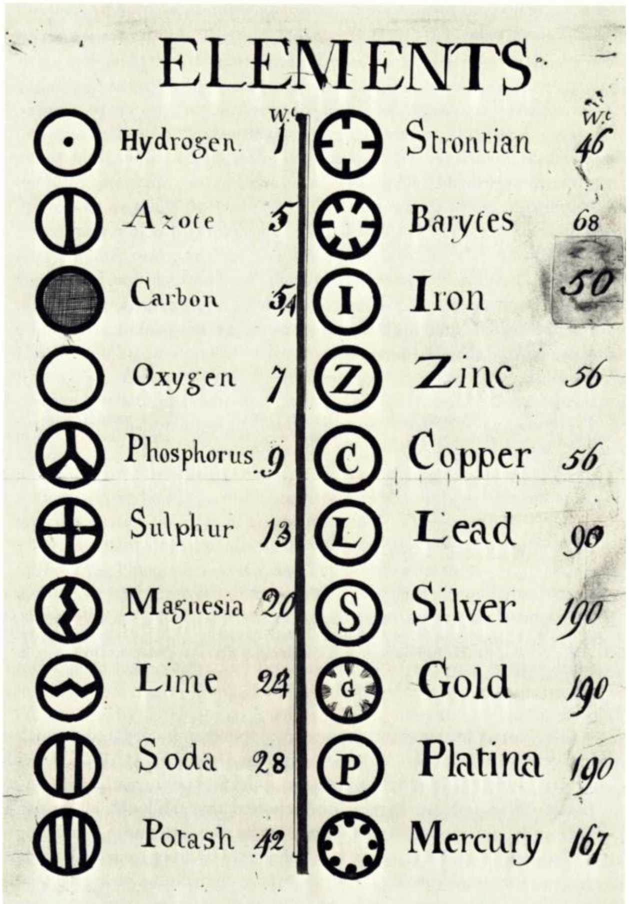
11 John Dalton, *New System of Chemical Philosophy,* Vol. I, 1st part. Bickerstaff, Manchester, 1808; Vol. I, 2nd part, Bickerstaff, Manchester, 1810 ; Vol. II, Bickerstaff, London, 1827.

1 atom of A + 2 atoms of B = 1 atom of D, ternary,
2 atoms of A + 1 atom of B = 1 atom of E, ternary,
1 atom of A + 3 atoms of B = 1 atom of F, quaternary,
3 atoms of A + 1 atom of B = 1 atom of G, quaternary,
etc. etc. [12]

And he adds what could be called a 'postulate of simplicity':

The following general rules may be adopted as guides in all our investigations respecting chemical synthesis:

1st 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.


ELEMENTS

	W.t		W.t
Hydrogen	1	Strontian	46
Azote	5	Barytes	68
Carbon	54	Iron	50
Oxygen	7	Zinc	56
Phosphorus	9	Copper	56
Sulphur	13	Lead	90
Magnesia	20	Silver	190
Lime	24	Gold	190
Soda	28	Platina	190
Potash	42	Mercury	167

***Figure 2:* Table of elements by John Dalton** *(from his* book New System of Chemical Philosophy, *1808). In the middle of each of the two columns we find the name of the element ('Lime' represents calcium, 'Soda' - sodium, 'Potash' - potassium); on the left we have symbols, and on the right are atomic weights as determined by Dalton at that time and later corrected by Avogadro so that they come very close to the values accepted today.*

It is notable that Dalton slightly changed his terminology; now he called 'atom' the smallest part of a substance, namely of an element or simple body,

12. John Dalton, *New System of Chemical Philosophy, op. cit.,* Vol. I, p. 213.

and of a compound body – a compound of two or more atoms (what we call a 'molecule'). Hence Dalton speaks of an 'atom' of water, according to him constituted by combination of an atom of oxygen and an atom of hydrogen. The proportion of masses of oxygen and hydrogen had been known since Lavoisier, who estimated it as 7 or 7½ to 1. Yet Dalton maintained it was 6 to 1, and concluded from this that an atom of oxygen is six times heavier than that of hydrogen (though in the second part of his book, published in 1810, he retained 7 to 1).[13] Step by step, a means to determine the relative masses of atoms emerged. The idea that matter is composed of atoms was no longer speculation devoid of practical consequences; Dalton in fact threw together the foundations of modern atomism.

GAY-LUSSAC (1808), EXPERIMENTAL RESULTS ON THE MIXED GASES

On 31st December 1808 Louis-Joseph Gay-Lussac gave a lecture at the Philomatic Society of Paris, soon published in *Mémoires de la Société d'Arcueil.*[14] At first glance his discovery seems incompatible with Dalton's theory. Gay-Lussac observed that, during chemical combination between two gases, their volumes are in direct proportionality, and that if the result is a gas, its volume is also directly proportional to the volumes of the reactants:

> *Compounds of gaseous substances with each other are always formed in very simple ratios, so that representing one of the terms by unity, the other is 1, 2, or at most 3 ... The apparent contraction of volume suffered by gas on combination is also very simply related to the volume of one of them.*

For example a litre of oxygen combines with two litres of hydrogen to produce two litres of water (in gaseous form); this is what we now express by the equation O_2 (one volume of dioxygen) + 2H2 (two volumes of dihydrogen) → 2H2O (two volumes of water). There are two very surprising results: the relations of volumes are in direct proportionality, yet the relation between the volumes of the reactants and the product of the reaction is also in direct proportionality. Moreover, as in the case of water, we start with three litres

13. Thomas Thomson, *New System of Chemistry,* vol. III, p. 442.

14. Louis-Joseph Gay-Lussac, 'Mémoire sur la combinaison des substances gazeuses les unes avec les autres ' *Mémoires de physique et de chimie de la société d'Arcueil,* Vol. II, p.207-237, 1809. *Société d'Arcueil* was founded by a group comprising the greatest savants of the time. Among them were: Pierre-Simon Laplace, Claude-Louis Berthollet, Jean-Baptiste Biot, Louis-Joseph Gay-Lussac, Alexander von Humboldt, Louis Jacques Thénard.

(for example) to get two. This contraction is a further mystery.

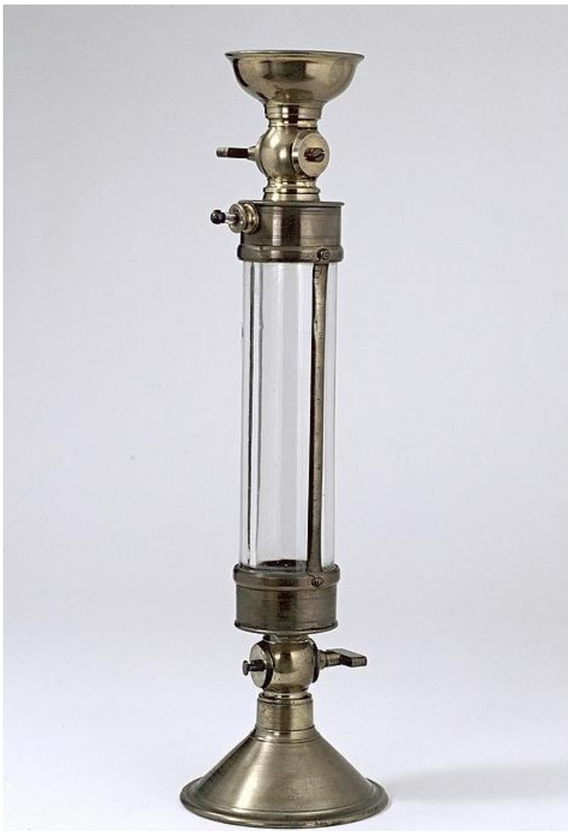


***Figure 3 :* Water eudiometer used by Gay-Lussac** *(photo by Bibliothèque de l'École polytechnique). An eudiometer is an instrument allowing the determination of the proportion of oxygen contained in atmospheric air by making it react with excess hydrogen to form water. The apparatus is placed in a water basin. Atmospheric air (or any analysed gas) is mixed with excess hydrogen and, after combustion triggered by a spark, the volume of oxygen contained in the air is determined by a one third decrease in the volume of the gas mixture accompanying the reaction.*

Gay-Lussac's memoir was received by Dalton with much scepticism, not because he doubted in the quality of measurements but because it seemed difficult to him to believe in the universality of the phenomenon. However, he admitted that the coincidence of experimental results with the simple figures was disturbing. Generally, Gay-Lussac's discoveries received a mixed reception: apart from Dalton, such renowned chemists as Berthollet and Berzélius were sceptical, whereas Thomas Thomson in England was rather persuaded. According to Jean Perrin, Gay-Lussac himself was more attached to experimental observation, without taking the trouble to draw consequences on atomic theory. Was it possible to reconcile Dalton's theory with Gay-Lussac's result, constant relation between masses with a simple relation between volumes?

THE FIRST HYPOTHESIS OF AVOGADRO

In 1809 Avogadro read Gay-Lussac's article. He also received the translation into French of *System of Chemistry*, a monumental treatise by the English chemist Thomas Thomson (1773-1852),[15] first published in 1802, and translated in 1809 by Jean Riffault[16] from the third edition of 1807. In this edition of the treatise, Thomson relates the conversations he had with Dalton and exposes, we could say as in premiere, the principles of a novel atomic theory of the latter.

Avogadro searches for a means to reconcile Gay-Lussac's result, the universal nature of which he does not doubt, with the atomic theory of Dalton. In his article, he starts by recalling Gay-Lussac's outcome:

> *M. Gay-Lussac has shown in an interesting Memoir [...] that gases always unite in a very simple proportion by volume, and that when the result of the union is a gas, its volume also is very simply related to those of its components.*

Avogadro makes a simple reasoning. First he remarks what seems obvious:

> *But the quantitative proportions of substances in compounds seem only to depend on the relative number of molecules which combine, and on the number of composite molecules which result.*

Avogadro deliberately puts himself, as Dalton, in the framework of atomic theory, but calls a 'molecule' what Dalton calls an 'atom', and a 'composite molecule' what we call 'molecule'. It was an important distinction, as we will presently see. To Avogadro a 'molecule' is the smallest part of a body.

Thus he continues his argument:

> *The first hypothesis to present itself in this connection, and apparently even the only admissible one, is the supposition that the number of integral molecules in any gases is always the same for equal volumes, or always proportional to the volumes.*

Avogadro calls an 'integral molecule' the molecule of a body - an element or a composite body. That is exactly what we now call a 'molecule'. This is the smallest possible part of any body. Avogadro states what is used to be called Avogadro's hypothesis. If the number of molecules in a given volume of gas is the same, regardless of the type of gas, the hypothesis allows an understanding that volumes of gas are by default in simple proportion: this is

15. Thomas Thomson, *System of Chemistry,* 5 vols., Edinburgh, Bell & Bradfute, 1807.
16. Thomas Thomson, *Système de chimie,* transl. Jean Riffault from the 3rd edition, introduction by Claude-Louis Berthollet, Paris, chez Mme veuve Bernard, 1809.

the proportion between the number of atoms forming the molecule.

From Avogadro's hypothesis to the notion of the mole and Avogadro's number N

Two distinct phenomena, one in chemistry and the other in physics, not wholly understood nor untangled at that time, must be grasped to make this leap across the ages:

- the principle of chemical reaction, namely the exchange by molecules of their constitutive atoms to form other molecules ($O_2 + 2H_2 \rightarrow 2H_2O$)
- the physical principle of ideal gases according to which, at a given temperature and pressure, the same number of gas molecules always occupies the same volume.

Dalton's hypothesis rather corresponded to the explanation of the chemical principle, Gay-Lussac's observations come under the physical principle. Avogadro would explain the latter by his first hypothesis and would advance the former thanks to his second hypothesis.

The first hypothesis of Avogadro explains the physical principle mentioned above:

At a temperature of 273.15K and under pressure of 1 atmosphere (101 325 Pa), the volume of a given quantity of gas molecules is constant. By convention, this quantity is the number of molecules of hydrogen in two grams of hydrogen gas (or of hydrogen atoms in a gram, this is the next equivalent this time of the second hypothesis of Avogadro): this quantity equals 6.022×10^{23} and is now called Avogadro's number. The volume occupied by one mole of gas molecules (this means 6.022×10^{23} molecules) is always equal to 22.414 litres.

Let us remark that one mole is a simple counting unit: it is to Avogadro's number as a 'dozen' is to 12.

We will notice that, with the help of his first hypothesis, Avogadro corroborated the experimental figures of gas density given by Gay-Lussac (end of I):

For example, since the numbers 1.10359 and 0.07321 express the densities of the two gases oxygen and hydrogen compared to that of atmospheric air as unity, and the ratio of the two numbers consequently represents the ratio between the masses of equal volumes of these two gases, it will also represent on our hypothesis the ratio of the masses of their molecules. Thus the mass of the molecule of oxygen will be about 15 times that of the molecule of hydrogen, or, more exactly as 15.074 to 1.

In the same way the mass of the molecule of nitrogen will be to that of hydrogen as 0.96913 to 0.07321, that is, as 13, or more exactly 13.238, to 1. [17]

THE SECOND HYPOTHESIS OF AVOGADRO

After the first hypothesis a great deal of the problem remained, with many thorny boughs. How could it be understood that the volume of gas produced in a chemical reaction can, in certain cases, be smaller than the sum of the volumes of gases that combine? This is the case with water, as we could see with Gay-Lussac. Dalton considered it absurd to imagine half-atoms, the term contradictory in itself since he supposed 'atom' to be the smallest, undividable part of an element.[18] And here Avogadro comes up with another hypothesis:

But a means of explaining facts of this type in conformity with our hypothesis presents itself naturally enough; we suppose, namely, that the constituent molecules of any simple gas whatever [...] are not formed of a solitary elementary molecule, but are made up of a certain number of these molecules united by attraction to form a single one.

Thus Avogadro explains in this phrase, probably not read attentively enough by his contemporaries, that if we admit that molecules, namely the smallest possible particles of gas, can be formed of two or more 'elementary molecules' (what we now call 'atoms'), everything becomes clear. In a chemical reaction the molecules divide into their constituents (atoms), which recombine themselves differently. This is the second idea, the second hypothesis of Avogadro. He takes the example of water and some other cases cited above:

Thus, for example, the integral molecule of water will be composed of a half-molecule of oxygen with one molecule, or what is the same thing, two half-molecules of hydrogen.

In the same way, we know that the volume of ammonia gas is twice that of the nitrogen which enters into it. M. Gay-Lussac has also shown that the volume of nitrous oxide is equal to that of the nitrogen which forms part of it, and consequently is twice that of the oxygen. Finally, nitrous gas, which contains equal volumes of nitrogen and oxygen, has a volume equal to the sum of the two constituent gases, that is to say, double that

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17. The term 'molecule' in its present meaning, namely that of an 'atom'. Avogadro gives 15.1 as the molar mass of oxygen and 13.2 as that of nitrogen. Present values are 16 and 14, respectively. The slight error stems from the experimental measurements of gas density (pressure and temperature should have been identical to verify the first hypothesis of Avogadro and to find out the correct molar masses).
18. 'Atom', from the Greek word '*a-tomos*', 'which cannot be cut', 'unbreakable'.

of each of them. Thus in all these cases there must be a division of the molecule into two.

Avogadro remarks that, in all cases he examined, 'there must be a division of the molecule into two', namely these gas molecules are diatomic, composed of two atoms. A truly remarkable conclusion! Based on Gay-Lussac's law and hypotheses, Avogadro manages to prove that the majority of gas molecules are composed of two or more atoms, and he also determines what we call the chemical formula of numerous substances, elements or chemical compounds, in the form accepted today: these two hypotheses are the foundation of present day chemical notation.

Avogadro's second hypothesis: the constitution of molecules in atoms

In modern language, Avogadro explains that a hydrogen molecule is composed of two atoms, like that of oxygen, which dissociate into two (atoms) to form two molecules of water, each composed of one atom of oxygen and two atoms of hydrogen, which we could write now as:

$$O_2 + 2H_2 \rightarrow 2H_2O$$

Likewise, he takes the example of ammonia and nitrogen monoxide (nitrous gas). In all cases he gives the correct formulation for these compound bodies. It is what we note today as:

$N_2 + 3H_2 \rightarrow 2NH_3$ (ammonia)

$N_2 + O_2 \rightarrow 2NO$ (nitrogen monoxide)

This is the conclusion of the second part of Avogadro's paper. In the first two parts he presented the great principles. In the next part he puts these to the test and shows how, in this way, the promise of the title, measuring the relative masses of different atoms, can be realised.

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Avogadro goes on in part III to rectify Dalton's formulations by using the second hypothesis. He starts with a comparison with Dalton's theory, which he, as he remarked at the bottom of the page, did not know otherwise but through the book of Thomson mentioned above:

Dalton, on arbitrary suppositions as to the most likely relative number of molecules in compounds, has endeavoured to fix ratios between the masses of the molecules of simple substances. Our hypothesis, supposing *it well-founded, puts us in a position to confirm or rectify his results from precise data, and, above all, to assign the magnitude of compound molecules according to the volumes of the gaseous compounds, which depend partly on the division of molecules entirely unexpected by this physicist.*

Avogadro puts his finger on what we termed the postulate of simplicity, namely: 'When only one combination of two bodies can be obtained, it must be presumed to be a *binary* one'. He calls it arbitrary, admitting at the same time that this is a natural hypothesis. Equipped with his new hypotheses he proposes 'to confirm or rectify' Dalton's results, by freeing himself from this postulate.

Avogadro applies his reasoning to water, and shows that it should be formed by a combination of one 'molecule' of oxygen and two 'molecules' of hydrogen. He goes on with two nitrogen oxides known at the time, and with carbon monoxide.

OXYMURIATIC ACID IS CERTAINLY AN ELEMENT

Part V of the article is devoted to what was then called 'muriatic acid', today known as hydrochloric acid, and 'oxygenated muriatic acid', or 'oxymuriatic acid', which is nothing else but chlorine. Chlorine was not recognised as an element; it was thought to be a combination of hydrochloric acid and oxygen. Yet the English chemist Humphrey Davy showed in 1810 it to be very doubtful that oxymuriatic acid contained oxygen:

One of the most singular facts that I have observed on this subject [...] is that charcoal, even when ignited to whiteness in oxymuriatic or muriatic acid gases, by the VOLTAIC battery, effects no change in them; if it has been previously freed from hydrogen and moisture by intense ignition in vacuo. This experiment which I have several times repeated, led me to doubt of the existence of oxygen in this substance.[19]

Avogadro draws from this a logical conclusion:

In the present state of our knowledge we must now regard this substance as still undecomposed, and muriatic acid as a compound of it with hydrogen.

By ascertaining oxymuriatic acid as an 'undecomposed' substance, he gives it the status of an element, which he got it right since it meant chlorine,

19. Humphrey Davy, 'Researches on the Oxymuriatic Acid, Its Nature and Combinations; And on the Elements of the Muriatic Acid. With Some Experiments on Sulphur and Phosphorus', *Philosophical Transactions of the Royal Society of London,* Vol. C, p.232, 1810.

and the molecule of muriatic acid, in other words hydrochloric acid, is composed of one atom of chlorine and one atom of hydrogen, as Avogadro indicates. He estimates the atomic mass of chlorine and finds it to be 33.36, in comparison with the actual value of 32.84 (if we take hydrogen mass as a unit). Avogadro obtained a result that was less than 2% off what it is now known to be.

We will not discuss the last two parts of Avogadro's article, in which he considers metals and combinations of salts with the aid of what he calls 'oxygenicity' – an idea he introduced in the paper[20] published in *Journal de Physique,* but which, however, did not survive.

AN ARTICLE DISREGARDED FOR MORE THAN HALF A CENTURY

In the conclusion of the article Avogadro insists on points of agreement with Dalton's theory:

> *It will have been in general remarked on reading this Memoir that there are many points of agreement between our special results and those of Dalton* [...] *This agreement is an argument in favour of our hypothesis, which is at bottom merely Dalton's system furnished with a new means of precision from the connection we have found between it and the general fact established by M. Gay-Lussac.*

To end, he wrote that maybe these ideas could be reconciled with those of Berthollet (because Berthollet did not believe the law of constant composition). By this perhaps he wanted to ease the 'revolutionary' impact of his ideas. Three years later, he publishes another article which only précised the results of the first in the light of new experimental data.[21]

This did not prevent his article from being disregarded for a very long time. The reason that it was hidden under a bushel was that many ideas were ahead of the time. Avogadro was a little known physicist, who never travelled beyond his native Piedmont, and who knew no great savants of the time and exchanged very little correspondence with any. It may be imagined that his article was not read with the great attention that it required, as it was undoubtedly not an easy read for his contemporaries. Moreover, his works are purely theoretical. He did

20. Amedeo Avogadro, 'Idées sur l'acidité et l'alcalinité', *Journal de Physique, de Chimie et d'Histoire naturelle,* Vol. LXIX, p. 142-148, 1809.
21. Amedeo Avogadro, 'Mémoire sur les masses relatives des molécules des corps simples, Ou densités présumées de leurs gaz, et sur la constitution de quelques-uns de leurs composés, pour servir de suite à l'*Essai* sur le même sujet, publié dans le *Journal de Physique*, juillet 1811.', *Journal de Physique, de Chimie et d'Histoire naturelle*, vol.LXXVIII, p. 131–156, February 1914.

not conduct experiments himself, and used the results published by others. This theoretical trait was not shared with any physicist or chemist of this age, which could have a negative impact on the way his subject was received. It is significant that the entry for 'atom' in the *Grand dictionnaire universel du XIX^e^ siècle*, published since 1866 by Pierre Larousse, does not even mention his name.

The French physicist André Marie Ampère (1775-1836), a nearly exact contemporary of Avogadro, made the same hypothesis, likewise the distinction between an atom (which he calls a 'molecule', like Avogadro) and a molecule (which he calls a 'particle'). His only known publication on this subject is in a letter to Berthollet[22] published in *Annales de Chimie* in 1814. In this letter, Ampère mentions a memoir on this subject, nearly finished, which he has no time to work on, so gives the extracts with essential points - very much akin to Avogadro's hypotheses.[23] He made yet another interesting supposition, that 'in order that this space [occupied by a 'particle'] may have three dimensions comparable between each other, a particle must consist of at least four molecules'.[24] This constraint makes the composition of particles much more complex, and the reading of the article becomes more difficult because of this. This idea has never been sustained. In France, reference to the Avogadro-Ampère hypothesis is often made. Both have come to the same conclusion in independent way, albeit with Avogadro having chronological priority. Ampère retreated under the barrage of criticism and never worked in this field again. This could also contribute to the side-lining of Avogadro's ideas.

AVOGADRO'S NUMBER AND THE MOLECULAR REALITY

It required more than 50 years before the revived Avogadro hypothesis

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22. André-Marie Ampère, 'Lettre à M. le comte Berthollet, sur la détermination des proportions dans lesquelles les corps se combinent d'après le nombre et la disposition respective des molécules dont leurs parties intégrantes sont composées', *Annales de Chimie* vol. XC, p. 43-86, 30 April 1914. XI. Letter from M. AMPERE to Count BERTHOLLET, on the determination of the proportions in which bodies are combined, according to the respective number and arrangement of the molecules of which their integrant molecules are composed', *Philosophical Magazine*, Series 1, Vol. XLV, Issue 201, 1815, p.42 (see *BibNum* analysis by P. Laszlo, October 2010)
23. At the bottom of the page, Ampère cites Avogadro: 'Depuis la rédaction de mon mémoire, j'ai appris que M. Avogadro avait fait de cette dernière idée la base d'un travail sur les proportions des éléments dans les combinaisons chimiques.' [Since the edition of my work I have learnt that Mr Avogadro had made this latter idea the basis of his work on the proportions of elements in chemical combinations]. Thus it seems he worked independently. Did he read *Journal de Physique* regularly? Or maybe he simply let the Avogadro's article pass because he did not know him?
24. Ampère thought that a molecule had a certain volume in space. But a molecule formed of one or two atoms is comprised within a plane, it has no other size than that of the atoms. This seemed impossible to him, hence the idea that molecules contain at least four atoms. This idea has not been entertained afterward.

could be related intimately with the atomic theory of matter, the founding father of which, for the modern era, remains Dalton.

Is matter composed of molecules, which are assemblages of atoms? Do these molecules exist in reality or are they purely theoretical speculations? These questions were the object of strong controversies for a good deal of the 19th century. In 1860, the first international congress of chemistry, convoked in Karlsruhe by the German chemist Friedrich August Kekulé (1829-1896) – known for having shown the tetravalence of carbon and the cyclic structure of benzene – did not distinguish between the supporters of the atomic hypothesis and its opponents, but the intervention of the Italian chemist Stanislao Cannizaro (1826-1910) was one of the factors that triggered a change of minds.[25] Cannizaro distributed copies of a summary of the chemistry course he taught at the University of Genoa,[26] which appeared in the Italian magazine *Il Nuovo Cimento* in 1858. He put forward an atomic theory like the one modified by Avogadro, and showed that it allowed for reporting all the results in chemistry in a coherent way. Step by step, atomic theory gained ground. In 1865 the Austrian physicist Joseph Loschmidt (1821-1895) determined for the first time the number of gas molecules in a given volume, with the use of the kinetic theory of gases. It was Jean Perrin who in 1909 proposed calling Avogadro's constant or Avogadro's number the number of molecules contained in 2 grams of hydrogen - which we today call one mole of hydrogen.[27] In this article he reported how he measured Avogadro's number by studying the Brownian motion of colloidal suspensions. He compared the result with those obtained by other totally independent methods, such as diffuse sky radiation, radioactivity measurements, elementary charge measurement, and black body radiation. With all these measurements giving consistent results, he could conclude:

> *I think it impossible that a mind, free from all preconception, can reflect upon the extreme diversity of the phenomena which thus converge to the same result, without experiencing a very strong impression, and I think that it will henceforth be difficult to defend by rational arguments a hostile attitude to molecular hypotheses, which, one after another, carry conviction* [...]

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25. *The Question of the Atom from the Karlsruhe Congress to the first Solvay Conference, 1860- 1911,* ed. Mary Jo Nye, Tomash Publishers, Los Angeles/San Francisco, 1984.

26. 'Lettera del Prof. Stanislao Cannizzaro al Prof. S. de Luca ; sunto di un corso di filosofia chimica, fatto nella R. Universita' di Genova', *Il nuovo cimento*, vol.VII, p. 321-366, 1858.

27. Jean Perrin, 'Mouvement brownien et réalité moléculaire', *Annales de Chimie et de Physique* 18, p. 5-114, September 1909. Brownian Movement and Molecular Reality, transl. F. Soddy, Taylor and Francis, London, 1910

In his iconic book *Les Atomes,* published in 1913 and which has been reissued many times,[28] Jean Perrin made a list of no less than 13 independent methods, all giving consistent results, nearing experimental certainty. Jean Perrin affirms:

> *Our wonder is aroused at the very remarkable agreement found between values derived from the consideration of such widely different phenomena. Seeing that not only is the same magnitude obtained by each method when the conditions under which it is applied are varied as much as possible, but that the numbers thus established also agree among themselves, without discrepancy, for all the methods employed, the real existence of the molecule is given a probability bordering on certainty.*

It is an irony of science that the moment atomic theory triumphed, the discovery and study of radioactivity revealed that atoms can disintegrate: that they are not immutable, indivisible and eternal as one may have thought. Perrin's conclusion is also ours:

> *But in achieving this victory we see that all the definiteness and finality of the original theory has vanished. Atoms are no longer eternal indivisible entities, setting a limit to the possible by their irreducible simplicity; inconceivably minute though they be, we are beginning to see in them a vast host of new worlds. In the same w ay the astronomer is discovering, beyond the familiar skies, dark abysses that the light from, dim star clouds lost in space takes aeons to span. The feeble light from Milky Ways immeasurably distant tells of the fiery life of a million giant stars. Nature reveals the same wide grandeur in the atom and the nebula, and each new aid to knowledge shows her vaster and more diverse, more fruitful and more unexpected, and, above all, unfathomably immense.*

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(February 2009)

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28. Jean Perrin, *Les Atomes,* Librairie Félix Alcan, Paris, 1913; reissue with the preface by Pierre-Gilles de Gennes, Champs/Flammarion, 1991.