Dalton's Long Journey from Meteorology to the Chemical Atomic Theory

Pier Remigio Salvi
Dipartimento di Chimica "Ugo Schiff", Università di Firenze,
via della Lastruccia 3, 50019 Sesto Fiorentino (FI), Italy

Email: piero.salvi@unifi.it

Abstract

The purpose of this paper is to review Dalton's contributions to science in various fields of research in relation to the first intimation of the chemical atomic theory. Early *"germs"* of his physical ideas may be found in the initial meteorological studies where water vapour is viewed as an *"elastic fluid sui generis"* diffused in the atmosphere and not as a species chemically combined with the other atmospheric gases. The next object of Dalton's attention was atmosphere itself. He discarded affinity between atmospheric gases as a possible cause of homogeneity and, making recourse to Newtonian *Principles*, considered the repulsive forces among particles. Experiments on the *"nitrous air test"* and on the diffusion and solubility of gases were instrumental to arrive at the chemical atomic theory. The slow, laborious, and persevering work of Dalton to get the first table of atomic weights is a fascinating piece of science which may be fully appreciated by referring to his laboratory notebook.

1 – Introduction

There has been in the years continuing interest on the genesis of the Dalton's chemical atomic theory [1-20]. According to Thomson[1] Dalton told him in a meeting that occurred in August 1804

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[1] see ref. [1], p. 289.

that he had come to the theory by speculating on the analyses of methane (*"carburetted hydrogen gas"*) and ethylene (*"olefiant gas"*) which indicate that for a given weight of carbon methane contained twice as much hydrogen as ethylene. This narrative cannot be trusted [4] given that the reported data were acquired in the summer of 1804, almost one year after the appearance, September 1803, of the first table of atomic weights in Dalton's notebook [4]. A second proposal[2] was advanced by William Henry, Dalton's closest friend, and his son, William Charles, Dalton's pupil. In conversation with them twenty-seven years after the event, Dalton stated he took inspiration for the atomic hypothesis thinking about the importance of Richter's table of equivalents. This is an equally doubtful assertion since (i) it is generally accepted [4,8-10] that Dalton was not aware of Richter's work in 1803 and (ii) in the table of atomic weights no entry refers to acids and bases, the subject of Richter's studies [8]. The young Henry himself expressed uncertainty about the validity of this recollection[3]. A third account, coming from a Dalton lecture held at the Royal Institution in 1810, was provided by Roscoe and Harden [4], responsible for the precious discovery and publication of Dalton's laboratory notebooks[4]. They point to the fact that the theory arose from considerations on the physical properties of gases rather than from experiments on multiple proportions. Unfortunately, this version comes from beliefs about atomic sizes and weights that Dalton proposed in 1804 or 1805 [5,9], rather than 1803 as claimed [4]. All this considered, it has been acutely remarked that a great scientist is not necessarily a good historian [5]. Successively, two positions emerged [5,8,9]. Shortly, the first [5] focuses the attention on the experiments performed by Dalton in 1803 relative to the reaction of nitric oxide with oxygen while the second [8,9] strongly advocates that the theory was first conceived to explain the differences in water solubility of various gases and that only in a second time Dalton realized the importance of application to chemical processes. More recently, other studies appeared [10-17]. In one of them [10] the initial Dalton's recognition of the novelty and significance of the theory from the chemical point of view is on the contrary stressed. In another study of particular interest, the nitric oxide/oxygen crucial experiment has been reproduced [12] and Dalton's pioneering observation of oxygen combination with one or two volumes of nitric oxide has been confirmed. Dalton also tested the nitrous oxide/oxygen reaction by eudiometry [13]. Finally, the influence of London atomists, such as William and Bryan Higgins, on Dalton has been hypothesized and the concept of atomic sizes reexamined [14-16].

On the other hand, it may be worthwhile to review the evolution of Dalton's scientific studies from meteorology [21] to the physics of atmosphere [22,23] and to the first papers on the atomic theory [24,25] through a detailed analysis of his contributions to these fields, as it is proposed in this work. In summary, the paper is organized as follows. In the next Section meteorological observations such as pressure measurements of water vapour, are presented and the conclusion is reached, in disagreement with the leading view at his times, that steam is an *"elastic fluid"* not chemically combined with the other atmospheric components [21]. Then at the end of the 18th century Dalton became interested in the nature of the atmosphere. To explain the atmospheric homogeneity, the theory of mixed gases was elaborated, and the enunciation was made of the law of partial pressures. This is the subject of Section 3 [22,23]. Gas diffusion and solubility were two experiments in agreement with the theory [26-28]. The two papers introducing the chemical atomic theory are reviewed in Section 4 [24,25]. In the first [24], by applying the *"nitrous air test"* to oxygen detection

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[2] see ref. [2], p. 63, 84-85.

[3] see ref. [2], p. 86.

[4] Dalton's laboratory notebooks were destroyed during the Second World War in a bombing over Manchester.

in the atmosphere, Dalton discovered the law of multiple proportions. In the second [25], the solubility of a series of gases in water was investigated and discussed as a purely physical process. The big difficulty, not amenable to the physical origin, was that the solubility varies considerably from one gas to another. Dalton's concern about this effect brought him to meditate about chemical atomism and eventually to present the first table of atomic weights. In Section 5 the main ideas developed on this issue and the criteria on which the table is based, are described with the fundamental help of his laboratory notebook [4]. The Conclusions Section includes a few comments on the outgrowth of the atomic theory. It is hoped that our approach, though of limited historical viewpoint, will not be without interest for scholars curious about the birth of modern chemistry.

2 – Meteorological studies

Dalton kept a constant interest in meteorology all along his life. In 1793 he published his first book, *Meteorological Observations and Essays*, the second edition appearing in 1834 [21]. The book, divided into two parts with appendixes, deals with various aspects of meteorology ranging from descriptive information on instruments such as barometers and thermometers, to data collection about atmospheric pressure and temperature and to reports on thunderstorms, winds, snow, and the like. Attention was also devoted to *Aurora Borealis* as a phenomenon related to the occurrence of magnetic matter in the atmosphere. Later, Faraday reported on *"atmospheric magnetism"* after his discovery of paramagnetic oxygen [29]. The second part of the book accounts for a few atmospheric processes; the sixth essay is concerned with evaporation, rain, and dew and shows *"germs"* of his physical ideas about vapour. Dalton states in the opening lines of the essay the two opposing views on vapour

"whether the vapour of water is ever chemically combined with all or any of the elastic fluids constituting the atmosphere [i.e., the view of Lavoisier and French chemists]*, or it always exists therein as a fluid **sui generis**, diffused among the rest"*[5]

and reports on pressure measurements of saturated water vapour at several temperatures in the range 80 – 212°F ($\approx$ 26 – 100°C). The results were interpreted in agreement with the second hypothesis although he acknowledged that the observed behaviour with temperature could have also suggested the first choice,

"the fact that a quantity of common air of a given temperature, confined with water of the same temperature, will only imbibe [dissolve] *a certain portion of the water, and that the portion increases with the temperature, seems characteristic of chemical affinity; but when the fact is properly examined, it will, I think, appear, that there is no necessity of inferring from it such affinity"*[6].

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[5] Ref. [21], p. 125.
[6] Ref. [20], p. 128.

There are comments on vapour saturation and condensation that are still valid. Suppose, he says, to reduce the pressure of 1 atm on vapour in equilibrium with water at 100ºC, to a smaller value, 1/10 atm. The new equilibrium temperature is t(ºC) < 100ºC, associated not only with the saturation pressure of 1/10 atm but also with the maximum vapour density at that temperature, called *"extreme density"* by Dalton. Then vapour, if mixed with dry air at t(ºC), will not condense until the pressure reaches 1/10 atm and the vapour density 1/10 that at normal ebullition (neglecting the weak dependence on temperature). Dalton concludes that *"there is no need to suppose a chemical attraction in the case"*.

The independence of the saturated vapour pressure on dry air addition is the second point of interest of the essay. The general, though not universal, view about water evaporation was in the opposite sense, i.e., it was argued that the water vapour is chemically combined with air and that only at the boiling temperature, 212ºF, and above the vapour takes the form of an elastic fluid, called steam [5]. The only contrary opinion was from Wallerius, which was able to evaporate water into a vacuum [18]. However, affinity remained a necessary factor for evaporation under open air, it was replied, since the pressure of the saturated vapour is much lower than one atmosphere at ordinary temperatures and then not sufficient to cause the escape from the liquid. In the appendix to the sixth essay, Dalton reports on pressure measurements at several temperatures on water placed into the vacuum of a barometer, confirming the values taken in the presence of air. Thus, vapour does not combine with air but rather

"the vapour of water (and probably of most other liquids) exists at all times in the atmosphere, and is capable of bearing any known degree of cold without a total condensation and the vapour so existing is one and the same thing with steam, or vapour of the temperature of 212ºF or upwards. The idea, therefore, that vapour cannot exist in the open atmosphere under the temperature of 212ºF unless chemically combined therewith, I consider as erroneous; it has taken its rise from a supposition, that air pressing upon vapour condenses vapour equally with vapour pressing upon vapour, a supposition we have no right to assume"[7].

Dalton concludes that *"the condensation of vapour exposed to common air does not in any manner depend upon the pressure of the air"*. It is fair to say that this statement is substantially, but not entirely, correct. In fact, as it may be seen in various physical chemistry textbooks [30-32] and educational papers [33], the pressure of saturated vapour in the presence of air increases with respect to that in a vacuum, the effect being related to the collisional pressing of nitrogen and oxygen molecules on the liquid inducing an additional transfer of water molecules in the gas phase [30,31]. The difference between pressures with and without air is significant only for added air at extremely high pressure while under the external pressure of 1 atm the two values are practically the same [33]. Summarizing, water vapour is viewed as an independent elastic fluid and evaporation is explained in mechanical terms without invoking a chemical combination of water with atmospheric gases. Maximum vapour pressure is associated with any given temperature, and water evaporates until this value is reached and no further.

3 – Theory of mixed gases

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[7] Ref. [21], p. 188.

The preliminary account of the theory was published in October 1801 [22] while the final expanded version is contained in the first of four *Experimental Essays*, read the same month, and printed one year later [23]. Dalton recalls that it was *"ascertained"* in the past that atmosphere behaves as *"a homogeneous fluid* [all its particles are of the same kind]*"* and that *"the elastic force of air was accurately as its density, in a given temperature* [i.e., at constant temperature the air pressure is proportional to density, as required by the Boyle law]*"*. Being Dalton strongly influenced by Newtonian mechanics he was eager to explain the result on the basis of the Newton's *Mathematical Principles of Natural Philosophy* [34]. To this purpose, he takes inspiration from proposition 23, book 2 of the *Principles*

"If the density of a fluid composed of particles that are repelled from one another is as the compression, the centrifugal forces [or forces of repulsion] of the particles are inversely proportional to the distances between their centres. And conversely, particles that are repelled from one another by forces that are inversely proportional to the distances between the centres constitute an elastic fluid whose density is proportional to the compression"[8].

As to the nature of the elastic fluid, Newton added cautiously at the end of the scholium accompanying the proposition

"Whether elastic fluids consist of particles that repel one another is, however, a question of physics. We have mathematically demonstrated a property of fluids consisting of particles of this sort so as to provide natural philosophers with the means with which to treat that question"[9]

On the authority of Lavoisier, an elastic fluid was thought to be a combination of matter, or material principle, with caloric [18]. Dalton conceived [4] the *"ultimate atoms of bodies"* as *"those particles which in the gaseous state are surrounded by heat; or they are the centres or nuclei of the several small elastic globular particles"[10]*. Since the caloric around the particles was postulated to be self-repelling [36], a plausible argument is provided for the supposed repulsion, putting apart the prudent warning from Newton. Dalton recalls that *"the atmosphere is not a homogeneous fluid; it is constituted of several elastic fluids"*, in sharp contrast with a basic principle of Aristotelian physics. But for an atmosphere of this kind, the Newtonian proposition is still valid? The question led him to discuss two critical points: (a) whether particles of different fluids repel each other as it happens for particles of the same fluid, and (b) why from their mixing a homogeneous fluid is formed. Dalton answers by taking advantage of the static model of fluid particles, of Newtonian origin [18], i.e., particles in fixed positions each with respect to any other. In this model, the pressure is due only to the repulsion between particles [19]. On expanding at a given temperature the interparticle distance increases, the repulsion weakens, and the pressure upon any particle lowers. On increasing the temperature at constant volume, the repulsion between particles increases [36] and the pressure goes up.

According to Dalton, when two fluids A and B are mixed four types of *"affections* [interactions]*"* may be guessed

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[8] Ref. [34], p. 697. The proof of the direct theorem in an updated version may be found elsewhere [35].
[9] Ref. [34], p. 699.
[10] Ref. [4], p. 27.

"1. The particles of one elastic fluid may repel those of another with the same force as they repel those of their own kind.

2. The particles of one may repel those of another with forces greater or less than that exerted upon those of their own kind.

3. The particles of one may possess no repulsive (or attractive) power or be perfectly inelastic with regard to the particles of another; and consequently, the mutual action of such fluids, or the action of the particles of one fluid on those of the other, will be subject to the laws of inelastic bodies.

4. The particles of one may have a chemical affinity, or attraction, for those of another."[11]

Dalton considers the four cases and concludes that only the third is consistent with atmospheric homogeneity. Suppose, he says, that *m "measures* [volumes]*"* of A and *n "measures"* of B are enclosed in two boxes having a common wall, under atmospheric pressure at a given temperature. Removing the wall, the total volume will be in the first three cases $(n + m)$. As to cases 1 and 2, if the two fluids have different *"specific gravities"*, the lightest would rise to the upper part of the vessel, due to the weaker gravitational attraction. The two fluids will separate in layers, forming what it may be called in our terms a two-phase fluid system. The pressure on any particle would be equal to one atmosphere. No two elastic fluids behave in this way [23]. On the contrary, since in the third case the repulsion between A and B particles is absent

"The two fluids, whatever their specific gravities may be, will immediately or in a short time, intimately diffused through each other, in such a manner that the density of each, considered abstractedly, will be uniform throughout; namely (calling the density of the compound, unity) that of A will be m/(n+m) and that of B = n/(n+m) ………... The pressure upon any one particle in this case will not be as the density of the compound, as before, but as the density of the particles of its own kind: that is, the pressure upon a particle of A will be equal [m/(n+m)]·30 inches of mercury; that upon a particle of B = [n/(n+m)]·30 inches; those pressures arising solely from particles of their own kind"[12]

The fourth case implies that after mixing *"a union of particles ensues"*. The product may be solid, liquid, or gaseous. For instance, *"when muriatic acid gas* [HCl] *and ammoniacal gas* [NH_3] *are mixed together in due proportion, a solid substance, muriate of ammonia* [NH_4Cl] *is formed, and the gases wholly disappear"*. When a gas is formed, the most probable effect is the volume reduction together with an increase of specific gravity and temperature, for instance *"when nitrous gas* [NO] *and oxygenous gas* [O_2] *are mixed in due proportion, the two unite and form a new elastic compound of greater specific gravity and consequently of less bulk, nitric acid gas* [NO_2]*"*. No evidence of chemical affinity has been reported mixing O_2 with N_2 and therefore *"this hypothesis fails equally with the other two"*. As a result of these considerations the structures of single atmospheric gases and their mixture are illustrated in **Fig. 1**, where *"in the compound atmosphere the same arrangement is made of each kind of particles as in the simple; but the particles of different kinds do not arrange at regular distances from each other; because it is supposed they do not repel each other"*. A law is stated, which is now known as Dalton's law of partial pressures:

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[11] Ref. [23], p. 536.
[12] Ref. [22], p. 242-243.

"When two elastic fluids, denoted by A and B, are mixed together, there is no mutual repulsion amongst their particles; that is, the particles of A do not repel those of B, as they do one another. Consequently, the pressure of whole weight upon any one particle arises solely from those of its own kind"[13].

On this basis Dalton makes remarkably advanced considerations. The four components of the atmosphere considered by Dalton (nitrogen, oxygen, water vapour and carbon dioxide) press on the surface of earth independently of each other so that the disappearance of any one of them does not affect the density and the pressure exerted by the others. Therefore, the definition of atmosphere by Lavoisier as *"a compound of all the fluids which are susceptible of vaporous or permanently elastic state in the usual temperature* [liquids, like water, undergoing evaporation or gases at ordinary temperatures]*, and under the common pressure"[14]* can be accepted only if the last five words are omitted. Second, even if all atmospheric fluids were eliminated, except aqueous vapour, little effect would result on the water evaporation, the only important factor being the pressure of saturated vapour at the given temperature. This was a strong argument against the prevailing idea that water was in liquid form at room temperature because of the atmospheric pressure on its surface.
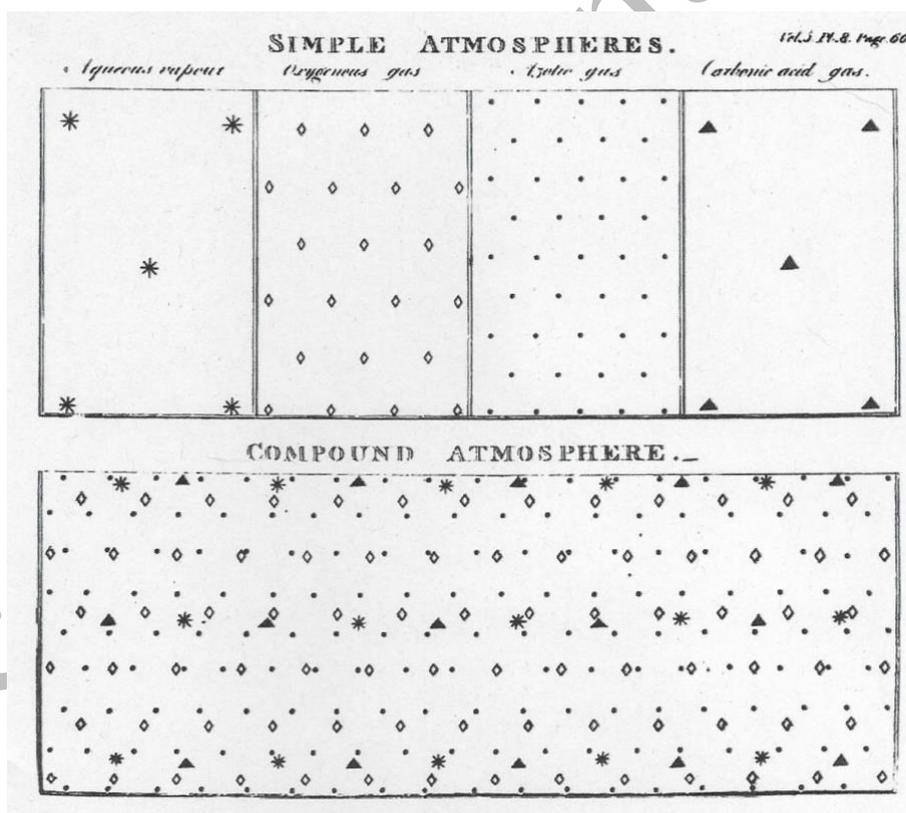

Fig. 1 – Dalton original plate [23] of simple (*"aqueous vapour, oxygenous, azotic, carbonic acid gases"*, upper) and mixed (*"compound"*, lower) atmospheres.

a – studies on gas diffusion and solubility in water under pressure

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[13] Ref. [23], p. 536.
[14] A. Lavoisier, *Traité de Chimie, 1789, i,* p. 31.

Two experiments support the theory of mixed gases [37,38]. In the first [37] (read January 28th, 1803, published in 1805) the gas diffusion is investigated: two gases are enclosed in two phials connected by a narrow vertical tube with the heavier in the lower phial. Such a simple set-up was kept *"in the state of rest"* as much as possible and the capillary tube, ten inches long, was *"not instrumental in propagating an intermixture from a momentary commotion at the commencement of each Experiment"*. Although Priestley had already shown that elastic fluids of different specific gravities do not separate in layers, with the heaviest in the lowest place [39], he nevertheless hypothesized that *"if two kinds of air, of very different specific gravities, were put into the same vessel, with very great care, without the least agitation that might mix or blend them together, they might continue separate, as with the same care wine and water may be made to do"*[15]. Dalton was aware that the outcome of his experiment, *"which seems at first view but a trivial one, is of considerable importance; as from it we may obtain a striking trait, either of the agreement or disagreement of elastic and inelastic fluids in their mutual action on each other"*, i.e., may corroborate or not the theory of mixed gases. Obviously, in the long run, all pairs of gases mix uniformly, CO_2 (*"carbonic acid gas"*, lower phial) with air, H_2, N_2 and NO (*"nitrous gas"*) and H_2 (upper phial) with air and O_2, thus establishing *"the remarkable fact that a lighter elastic fluid cannot rest upon a heavier"*.

The second experiment is concerned with gas dissolved in water under pressure. The study reports on what is now known as Henry's law [38]. It is in our opinion worth outlining the experimental apparatus, as an example of the chemical expertise of Dalton's times. As shown in **Fig. 2**, the two legs (A and B) of a syphon tube, A being a small, graduated bottle and B an ordinary glass tube open to the atmosphere, are filled with mercury up to the complete replenishment of A and rise at the corresponding level in B. A given quantity of water and a volume of gas may be poured into the bottle through the stopcock *a* when the stopcock *b* situated between the two legs is opened to allow mercury to run out. Then, with *a* closed the level of mercury in both legs is adjusted to the same height so that the gas is under atmospheric pressure. Let us suppose now to add mercury in B to form a column 76 cm higher than the A level. The gas inside the bottle is compressed to two atmospheres and its volume is found to be half that previously occupied. The bottle is vigorously agitated, the absorption of gas takes place and the level of mercury in the bottle rises. To reestablish the pressure difference between A and B it is necessary to add mercury in B: in these conditions, the gas pressure is again two atmospheres and the volume of gas absorbed by water is exactly equal to the mercury added in the last step. With this apparatus Henry determined the solubility of gases such as *"carbonic acid"*, *"sulphuretted hydrogen [H_2S]"*, *"nitrous oxide [N_2O]"*, *"oxygenous and azotic gases"* in water up to three atmospheres. The most significant result was that *"under equal circumstances of temperature water takes up in all cases the same volume of condensed gas as of gas under ordinary pressure"*. To exemplify, if a given quantity of water absorbs 10 ml of a gas at p = 1 atm, it will absorb 10 ml of the same gas at p = 2 atm. But the volume absorbed at p = 2 atm, if expanded to p = 1 atm, would be double that absorbed at p = 1 Atm, or in more general terms

"water takes up of gas condensed by one, two, or more additional atmospheres, a quantity which, ordinarily compressed, would be equal to twice, thrice, etc. the volume absorbed under the common pressure of the atmosphere"[16]

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[15] cited in ref. [37], p. 260.
[16] Ref. [38], p. 42.

Then, the weight of the gas dissolved at p = 2 atm will be double that at 1 atm and the law takes the more familiar enunciation that the absorbed gas weight is proportional to the incumbent gas pressure [19]. Dalton realized that this behaviour could not be explained in terms of chemical combination of dissolved gas with water, given that the gas is kept in water only due to the gas pressure. This point is clearly attested by Henry in the Appendix [40] of the paper with the following words

"The theory which Mr. Dalton has suggested to me on this subject, and which appears to be confirmed by my experiments, is, that the absorption of gases by water is purely a mechanical effect, and that its amount is exactly proportional to the density of the gas, considered abstractedly from any other gas with which it may accidentally be mixed"[17].
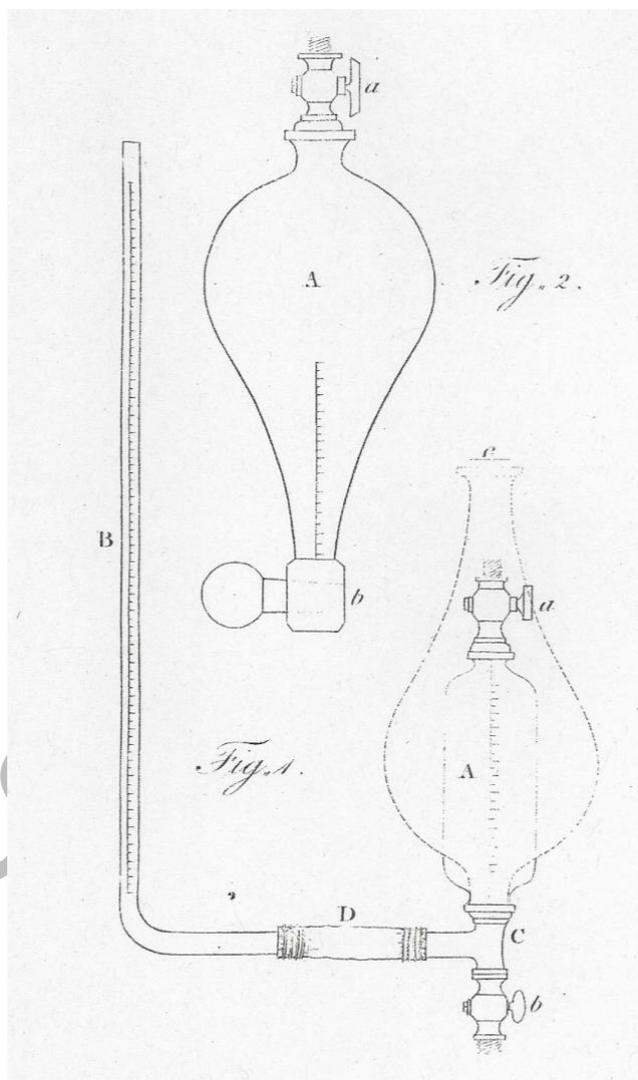

Fig. 2 – Solubility of gases in water: Henry's experimental apparatus for measurements under pressure from ref. [38]. The larger vessel A was used with *"less condensible gases"*.

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[17] Ref. [40], p. 274.

b – theory of mixed gases: historical perspective and limits

After having reviewed the theory of mixed gases, we feel appropriate to refer shortly to the underlying topic, i.e., forces acting between *"ultimate particles"*, and specifically on the theory proposed by the mathematician and astronomer Roger Boscovich [41]. Then, we will make a few general comments on the Dalton theory. Let us start by saying that in the 18th century matter was considered to consist of discrete particles or *"corpuscles"* supposed to be stationary, namely motionless and not colliding [35]. The concept of potential energy was unknown, and the physical world was described in terms of mechanical forces between particles [35]. Of great interest for the originality of the model was the Boscovich theory of oscillatory force. At the planetary and interstellar scale, the gravitational force of attraction, depending on distance as $\frac{1}{r^2}$, dominates. As r recedes, the force is increasingly negative and particles accelerate when approaching each other but at sufficiently short distances, to account for the fact that matter cannot disappear into itself, particles must slow down and then, as r decreases, a repulsive force is supposed to emerge leading first to the inversion of the force from negative to positive and for $r \to 0$ to a repulsion force arbitrarily high. If these two forces were the only ones in action, a single homogeneous solid would result at equilibrium, i.e., at the inversion point. Boscovich assumed that between the two extremes, $r = 0$ and $r \to \infty$, additional inversion points occur so that the force oscillates alternatively, depending on the experimental conditions [42]. For instance, the caloric fluid, capable of flowing in and out of all matter, was known to be self-repulsive and then responsible for the repulsion force suggested by the Boyle law. The point at which the gravitational and caloric forces are equal constitutes a second inversion point which determines the static equilibrium in gases. In summary, starting from exceedingly small distances the force oscillates from highly repulsive to attractive (in solids) to repulsive (in gases) and again to attractive at exceptionally large distances.

Going to the second point, it has been wisely noted [18] that the subject of mixed gases can be correctly treated only after admitting that the particles are in motion and not rigidly located at fixed positions. In the absence of the kinetic theory of gases[18] and not resorting to the thermodynamic notion of entropic increase to justify why elastic fluids of whatever density occupy all the available volume, Dalton ascribed to the supposed repulsion between particles the tendency of gases to expand in the whole space. Now we know that gaseous particles weakly attract each other, as it was established by the van der Waals equation for non-ideal gas, but only seventy years later. Thus, a gas must be rather regarded as composed of particles in motion exerting weak attraction forces on each other. All these considerations give evidence of the extraordinary degree of ingenuity of Dalton who, though lacking essential theoretical instruments, arrived at the law of partial pressures by taking only advantage of a bold *ad hoc* hypothesis, *"every gas is a vacuum to every other gas"*, as expressed concisely and brilliantly by Henry [44].

4 – Stepping into the chemical atomic theory

As already noted in the Introduction, the narratives concerning the origin of Dalton's atomic theory go back to Dalton himself [1,2,4]. In later years they were critically reviewed, and alternative

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[18] It should be however recalled that the concept of particle motion was at the centre of the Bernoulli equation obtained in 1738 [43], $pV = \left(\frac{1}{3}\right)nmv^2$, where p is the pressure defined as the force f, due to the collisions in unit time on the container wall, over its area A, n the number of particles, each of mass m and mean velocity v.

explanations were proposed [5,8-10,12,13]. In this Section, we approach the atomic theory taking into consideration the two basic papers [24,25] upon which the theory is founded with the essential support of the Dalton laboratory notebook [4].

a – Experimental Enquiry into the Proportion of the Several Gases or Elastic Fluids, constituting the Atmosphere [24]

The essay under heading was read at the meeting of the Literary and Philosophical Society of Manchester on November 12th, 1802; the publication was delayed until November 1805. Starting from the consideration, based on the theory of mixed gases, that the pressure of a fluid is the same as a single component or in a mixed state, depending only on density and temperature, Dalton determines (i) the pressure of each *"simple atmosphere"* in the *"compound atmosphere"* and then the volume percent of each gas, (ii) the weight percent in a given volume and (iii) the dependence of these properties upon the height above the earth's surface. The gases under examination are *"azotic, oxygenous, aqueous vapour, and carbonic acid"*, which were detected in any atmospheric region by means of the analytical methods known at his time.

Beginning with (i), the reactions for oxygen detection were carried out over water and *"if it should appear that by extracting the oxygenous gas from any mass of the atmospheric air, the whole was diminished $\frac{1}{5}$ in bulk, still being subject to a pressure of 30 inches of mercury* [one atmosphere]*; then it ought to be inferred that the oxygenous atmosphere presses the earth with a force of 6 inches of mercury"[19]*. The reagents were *"nitrous gas [NO]"*, *"liquid sulphuret of potash and lime* [water solutions of K_2S and CaS, the reaction being $2HS^- + O_2 \rightarrow 2S + 2OH^-$]*"*, *"hydrogen gas [$2H_2 + O_2 \rightarrow 2H_2O$]"* and *"burning phosphorous [$P_4 + 5O_2 \rightarrow 2P_2O_5$]"*. Dalton reports volumetric estimates of air reduction only for the first and third reaction, specifying that when all these reactions are conducted *"skilfully"* no difference between results occurs. For instance, by firing 60 *"measures"* of hydrogen with 100 of common air, the final volume is again 100 with complete oxygen disappearance. From these data he found that the oxygen volume is 21 *"measures"* and then the oxygen pressure 6.3 inches. We may suppose that the calculation was done along the following lines (in present-day notation)

$$(a) \; V_A + V_{O_2} = 100 \quad (b) \; V_{H_2,r} + V_{H_2,unr} = 60 \quad (c) \; \frac{V_{H_2,r}}{V_{O_2}} = 1.85 \quad (d) \; V_A + V_{H_2,unr} = 100$$

where V_A is the volume of all gases in common air except oxygen and $V_{H_2,r}$, $V_{H_2,unr}$ the reacted and unreacted parts of the total hydrogen volume. The ratio (c) is the value measured by Dalton [24], 1.85, (the theoretical value 2 was unknown). Solving for V_{O_2} he obtained $V_{O_2} = 21$.

the "nitrous air test"

Greater attention must be deserved to the oxygen detection with NO. After the discovery by Hales pouring nitric acid on Walton pyrites [45] the reaction was studied in detail by Priestley in 1772 [46]. Since then, many chemical investigators (including Dalton) used this reaction to estimate the purity or *"goodness"* of air. Priestley found that combining any kind of metals then known (except zinc)

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[19] Ref. [24], p. 246.

with *"spirit of nitre* [nitric acid]*"* an *"air"*, that he called *"nitrous air"*, evolved forming deep *"red fumes"* in the presence of common air. In actual terms the reaction is

$$2NO + O_2 \rightarrow 2NO_2$$
"nitrous air"　　　*"red fumes"*
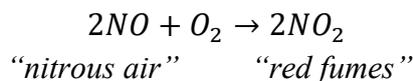
and since NO_2 is easily dissolved in water (while NO is not) it follows that, if correctly chosen volumes of NO and O_2 are mixed over water, all gases disappear. Starting with common air Priestley always found a large amount of residual gas, which turned out to be the smallest when two volumes of common air were mixed with one of NO. In this case, the residue was about 1.8 volumes and the remarkably high contraction of 1.2 volumes corresponded to the volume of added NO plus 20%. The degree of volume reduction was then $\sim \frac{1}{3}$. He noted with satisfaction that this contraction

*"is peculiar to common air or air fit for respiration; and …. very nearly, if not exactly, in proportion to its fitness for this purpose; so that by this means the **goodness of air** may be distinguished much more accurately than it can be done by putting mice or other animals, to breathe in it ….. a most agreeable discovery to me"*[20].

On the contrary, no reaction with NO was observed for air *"unfit for respiration"* such as fixed air (CO_2) or inflammable air (H_2) so that their *"goodness"* is zero. Intermediate degrees of reduction between zero (no reaction) to $\sim \frac{1}{3}$ (reaction of 1 volume of NO and 2 volumes of common air) represent intermediate degrees of *"goodness"*. Priestley proudly stated that *"we are in possession of a prodigiously large scale* [i.e., $0 - \frac{1}{3}$] *by which we may distinguish very small degrees of difference in the goodness of air"*.

Going now back to the Dalton paper, he found that the reacting volumes were strongly dependent on the experimental conditions. In fact, after preparing *"nitrous gas"* adding the water solution of nitric acid to copper or mercury (point 1), he says in the successive points

"2. If 100 *measures of common air be put to* 36 *of pure nitrous gas in a tube* $\frac{3}{10}$ *of an inch wide and* 5 *inches long, after a few minutes the whole will be reduced to* 79 *or* 80 *measures and exhibit no signs of either oxygenous or nitrous gas.*
3. If 100 *measures of common air be admitted to* 72 *of nitrous gas in a wide vessel over water, such as to form a thin stratum of air, and an immediate momentary agitation be used, there will, as before, be found* 79 *or* 80 *measures of pure azotic gas for a residuum.*
4. If, in the last experiment, less than 72 *measures of nitrous gas be used, there will be a residuum containing oxygenous gas; if more, then some residuary nitrous gas will be found"*[21]

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[20]Ref. [46], p. 114, bold letters, our addition.
[21]Ref. [24], p. 249.

These data indicate that a given volume of oxygen (making part of the common air) reacts with another of NO or its double. This implies the law of multiple proportions. The conclusion is expressed by Dalton with the following significant words

*"These facts clearly point out the theory of the process: the elements of oxygen may combine with a certain portion of nitrous gas, or with twice that portion, but with no intermediate quantity. In the former case **nitric** acid $[2NO + O_2 \rightarrow 2NO_2]$ is the result; in the latter **nitrous** acid $[4NO + O_2 \rightarrow 2N_2O_3]$: but as both these may be formed at the same time, one part of the oxygen going to one of nitrous gas, and another to two, the quantity of nitrous gas absorbed should be variable; from 36 to 72 per cent for common air…. In fact, all the gradation in quantity of nitrous gas from 36 to 72 may actually be observed with atmospheric air of the same purity; the wider the tube or vessel the mixture is made in, the quicker the combination is effected, and the more exposed to water, the greater is the quantity of **nitrous** acid and the less of **nitric** that is formed"*[22].

There has been much debate among science historians about when Dalton obtained the results of points 2 and 3. These, if presented at the reading date, November 12th, 1802, would mean that the law of multiple proportions was discovered long before the proposal of the atomic theory (which is, as it is well known [4], September 6th, 1803). The Dalton notebook [4], from November 1802, the date of the earliest records on his laboratory activity, until the end of 1803, supports the idea that both the experimental results and the discussion were made at a time later than November 1802. For instance, Dalton writes, March 21st, 1803, *"Nitrous gas – 1.7 or 2.7 may be combined with oxygen, it is presumed"*[23]. Second, on April 1st, 1803, several experiments are listed on *"nitrous gas"* and common air in relation to the higher absorption of the reactant when the mixture is rapidly formed but the record ends with the doubtful question *"Query, is not nitrous air decomposed by the rapid mixture?"*. At that date, six months after November 1802, Dalton had not reached the well-defined conclusions expressed in the paper [4]. The discrepancy between presentation and publication has been explained [4] by the fact that Dalton, as Secretary of the Manchester Literary and Philosophical Society since 1800, had many opportunities to revise the work according to his latest findings. Further, the numbers quoted in points 2 and 3 of the paper were written in the notebook at an undetermined date between October 10th and November 13th, 1803, more than one month after the first appearance of the atomic weight table [4].

However, Dalton in some experiments before September 1803 had noticed a simple ratio for the volumes of *"nitrous gas"* reacting with a given volume of oxygen. The notebook reports, August 4th, 1803, that *"it appears, too, that a very rapid mixture of equal parts com. air and nitrous gas, gives* 112 *or* 120 *residuum. Consequently, that oxygen joins to nit. gas sometimes* 1.7 *to* 1 *and at other times* 3.4 *to* 1 [the theoretical ratios, unknown to Dalton, for the formation of nitric and nitrous acid, are $2:1$ and $4:1$, respectively]*"*[24]. This extract paved the way for the proposal [5] that Dalton,

[22]Ref. [24], p. 250.

[23] Ref. [4], p. 34. The two ratios, $1.7:1$ and $2.7:1$, are narrow tube and wide vessel values, respectively.

[24] Ref. [4], p. 38. A possible justification of the second ratio, $3.4:1$, may be derived as follows. The three equations to be considered are (a) $V_A + V_{O_2} = 100$; (b) $V_{NO,r} + V_{NO,unr} = 100$; (c) $V_A + V_{NO,unr} = 112$, where A denotes, as usual, all atmospheric gases except oxygen and $V_{NO,r}$ and $V_{NO,unr}$ are the reacting and excess volumes of NO. Taking from previous experiments as a reasonable approximation of the oxygen volume $V_{O_2} = 20$ we have $V_{NO,unr} = 32$; $V_{NO,r} = 68$ and then $\frac{V_{NO,r}}{V_{O_2}} = 3.4$. The same calculation with 120 residuum gives $\frac{V_{NO,r}}{V_{O_2}} = 3$.

pondering about the significance of the $2:1$ ratio of the reacted *"nitrous gas"* under different conditions, made the bold generalization, going from the particular NO reaction to the law of multiple proportions and then to the chemical atomic theory, which would have appeared within one month. In other words, here the suggestion is that the atomic theory was derived from the law of multiple proportions [5]. This view has been subject in the following years to a strong criticism emphasizing the experimental difficulties to replicate these ratios even when the reaction was carried out with the updated instrumentation available to researchers more than one century later [7,8]. For instance, it has been pointed out that, out of many reaction trials personally performed, few of them gave a ratio reasonably approximating $3.4:1$, the most difficult to replicate [8]. But, in contrast, a successful reconstruction of the experiment has been recently reported, where the narrow tube value, $1.7:1$, has been confirmed and the $3.4:1$ ratio justified observing that gas-phase and dissolved oxygen in the wide water vessel are involved when NO is in excess with respect to O_2 [12]. It has been added [12] that if the reaction is complete, i.e., in the presence of a sufficient amount of water, all excess NO is consumed and any NO/O_2 ratio greater than $2:1$ may be obtained; then Dalton carried out the reaction optimizing the experimental conditions to achieve the desired result, as it is evident comparing the notebook entries of March 12th and August 4th. Thus, the plausible conclusion was that Dalton discovered the first example of the law of multiple proportions having already in mind the implications of the atomic theory [12].

For completeness, it remains to report on the other points discussed in the paper. The pressures of water vapour and *"carbonic acid"* [CO_2] in the atmosphere were determined by means of the analytical methods known at that time. Dalton took advantage of the pressure diagram of saturated water vapour with temperature, already determined by himself and reported in ***Meteorological Observations and Essays***. It was enough to measure the dewpoint temperature of the vapour: the pressure of this vapour in the atmosphere coincides with that of the saturated vapour at dewpoint temperature[25]. Then, Dalton analyzed the amount of CO_2 by adding *"lime-water"* [saturated water solution of $Ca(OH)_2$] to precipitate atmospheric CO_2 contained in a bottle with a capacity of *"102400 grains of rain water [$\approx 7L$]"*. He found that *"102400 grains measures of common air contain 70 of carbonic acid"*. Going to point (ii) of the paper, Dalton, using densities from Lavoisier and Kirwan (N_2 and CO_2), Davy (O_2) and himself (H_2O vapour), arrived at the gravimetric percent composition of the air from volumetric data. Pressure (in *"inches of mercury"*) and percent of each component resulted to be: *"azotic gas"* 23.36, 75.55%; *"oxygenous gas"* 6.18, 23.32%; *"aqueous vapour"* 0.44, 1.03%; *"carbonic acid gas"* 0.02, 0.10%. As to point (iii), it was found that at higher altitudes the atmospheric oxygen decreases with respect to the other gases but only slightly. From this Dalton concluded that *"at any ordinary heights the difference in the proportions will be scarcely if at all perceptible"*.

b – On the Absorption of Gases by Water and Other Liquids [25]

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[25] Dalton had already given the definition of dewpoint in the following terms [47]:*"whatever quantity of aqueous vapour may exist in the atmosphere at any time, a certain temperature may be found, below which a portion of that vapour would unavoidably fall or be deposited in the form of rain or dew, but above which no such diminution could take place, chemical agency apart. This point may be called the **extreme temperature** [i.e., dewpoint] of vapour of that density. Whenever any body colder than the extreme temperature of the existing vapour is situated in the atmosphere, dew is deposited upon it"*.

This paper was read in front of a selected audience of nine members and friends at the meeting of the Literary and Philosophical Society of Manchester held on October 21st, 1803 and printed on the Manchester Memoirs of the Society in November 1805, following the paper of the previous subsection. The experiments on gas solubilities in water were prompted by Henry's studies in this field and represent a big part of Dalton's work in the last months of 1802, from January to March 1803 and in August of the same year [4]. Both men interpreted the results as being due to a mechanical, rather than to a chemical effect, arising only from the pressure of the absorbed gas and independent of the presence of any other gas [40]. Fifteen experiments, numbered as *"articles"* in the paper, are presented, the most significant being undoubtedly the second:

"If a quantity of water thus freed from air be agitated in any kind of gas, not chemically uniting with water, it will absorb its bulk of the gas [CO_2, H_2S, N_2O]*, or otherwise a part of it equal to some one of the following fractions, namely, $\frac{1}{8}$* [C_2H_4]*, $\frac{1}{27}$* [O_2, NO, CH_4]*, $\frac{1}{64}$* [H_2, N_2, CO]*, &c. these being the cubes of the reciprocals of the natural numbers 1, 2, 3, &c. or $\frac{1}{1^3}$, $\frac{1}{2^3}$, $\frac{1}{3^3}$, $\frac{1}{4^3}$, &c. the same gas always being absorbed in the same proportion ……………: – It must be understood that the quantity of gas is to be measured at the pressure and temperature with which the impregnation* [saturation] *is effected."*[26]

It has been noted [8] that Dalton often indulged in the search of simple mathematical relations even in the presence of experimental values affected by a large error such as those relative to solubility measurements of the period January – March 1803 [4]. The difficulties encountered in data acquisition are evident in this long paragraph of the paper:

"In my Experiments with the less absorbable gases, or those of the 2d, 3d, and 4th classes, I used a phial holding 2700 grains of water, having a very accurately ground-stopper; in those with the more absorbable of the first class, I used an Eudiometer tube properly graduated and of aperture so as to be covered with the end of a finger……… [which] *was applied to the end and the water within agitated; then removing the finger for a moment under water, an additional quantity of water entered, and the agitation was repeated till no more water would enter, when the quantity and quality of the residuary gas was examined. In fact, water could never be made to take its bulk of any gas by this procedure; but if it took $\frac{9}{10}$, or any other part, and the residuary gas was $\frac{9}{10}$ pure, then it was inferred that water would take its bulk of that gas. The principle was the same in using the phial; only a small quantity of the gas was admitted, and the agitation was longer"*[27].
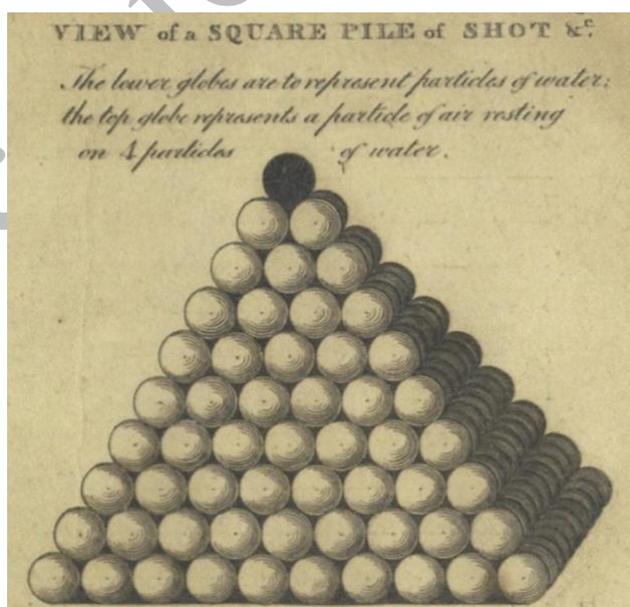
But by March 6th, 1803, he trusted data on hydrogen, nitrogen and oxygen [4] since *"it now appears more than probable that in all cases hydrogen and azotic gases in water have their particles 4 times the distance that they have incumbent $= \frac{1}{64}$ or 1.5625 per cent, and oxygen gas 3 times $= \frac{1}{27}$ density $= 3.7$* [per cent]*"*. To our opinion, much of the credit for the better-defined relation of solubilities to inverse cubes of natural numbers belongs to the more reliable Henry data [39], as Dalton fairly acknowledges with these words: *"by the reciprocal communication* [between Dalton and Henry]

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[26] Ref. [25], p. 271.
[27] Ref. [25], p. 280.

since, we have been enabled to bring the results of our Experiments to a near agreement; as the quantity he has given in his appendix to that paper nearly accord with those I have stated in the second article". On October 21st, 1803, Dalton had sound data for the three gases (and for *"carbonic acid"* and *"nitrous oxide [N_2O]"* [4,8]). The data relative to *"carburetted hydrogen"* and (probably) *"olefiant gas"* were obtained at a later date [4,8,18].

Dalton explains the solubility of gases in water in *"mechanical"* terms saying that *"all gases that enter into water and other liquids by means of pressure, and are wholly disengaged again by the removal of that pressure, are mechanically mixed with liquids, and not chemically combined with it"*[28]. As already outlined in the past Section, the gaseous particles were thought to form an array of hard-packed spheres repelling each other both in water and out of it; further, the gas was retained in water only by the pressure of particles of the same kind and *"water has no other influence in this respect than a mere vacuum"*. Dalton asks in the notebook [4]: *"is it not two atmospheres pressing one against the other?"* of which one is the *"atmosphere"* of the gas pressing on water and the other the hypothetical *"atmosphere"* of the dissolved gas. The two *"atmospheres"* have different densities and the ratio is given by the reciprocal of cubes of natural numbers. For instance, oxygen in water is less dense than out by $\frac{1}{3^3} = \frac{1}{27}$; the same ratio for nitrogen is $\frac{1}{4^3} = \frac{1}{64}$. Thus, the distance between adjacent dissolved particles is a multiple of the distance in the atmosphere, *"in oxygenous gas, &c. the distance is just three times as great within as without; and in azotic, &c. it is four times."*[29]. Some drawings are attached to the paper, to make more explicit Dalton's physical theory of gas absorption. In *"View of a Square Pile of Shot"*, **Fig. 3**, squares of packed spheres (white, water particles) are pressed by the upper sphere (black, a gas particle) and the pressure is distributed among the water particles, first on 4, then from 4 to 9, from 9 to 16, etc., until the next lower particle of absorbed gas is reached. Since in **Fig. 3** the ratio of the distance between gas particles and between water particles is supposed to be 10:1 the final pressure is distributed among 100 water particles and *"[since] in the same stratum each square of 100 [has] its incumbent particle of gas, the water below this stratum is uniformly pressed by the gas, and consequently has not its equilibrium disturbed by that pressure"*[30].

VIEW of a SQUARE PILE of SHOT &c.

the lower globes are to represent particles of water: the top globe represents a particle of air resting on 4 particles of water.

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[28] Ref. [25], p. 283.
[29] Ref. [25], p. 281.
[30] Ref. [25], p. 284.

Fig. 3 – A particle of gas (black sphere) pressing particles of water (white spheres), from ref. [25].

In *"Profile View of Air in Water"*, **Fig. 4**, right, the oxygen dissolved in water is considered. Its pressure amounts to $\frac{1}{27}$ of the incumbent pressure and, as Dalton points out, this pressure is exerted on the container walls and on the gas above the water, not on water. At equilibrium, atmospheric oxygen presses the dissolved portion by the same pressure, $\frac{1}{27}$, and the remaining, $\frac{26}{27}$, is the pressure of the gas on the water's surface. There is repulsion between the two strata of oxygen just adjacent to this surface, though much smaller, $\frac{1}{27}$, than between particles in the atmosphere. Being the repulsion inversely proportional to the distance, this means that the two strata must be apart 27 times the distance of particles in the atmosphere. Applying the same line of reasoning to N_2 and H_2, the distance between the two strata increases to 64 times, as seen in **Fig. 4**, left.
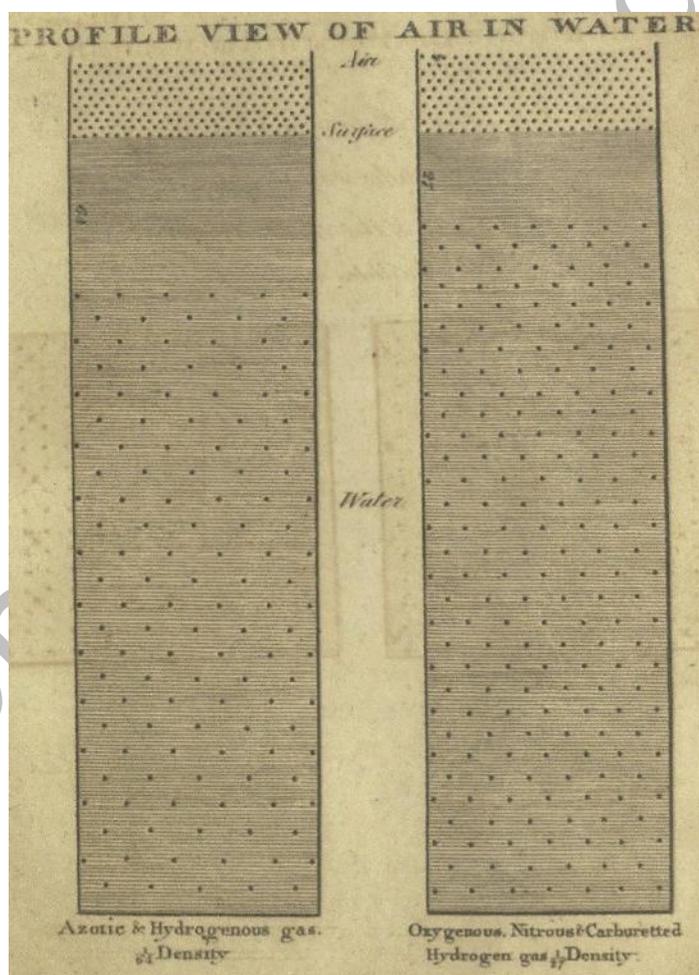

Fig. 4 – The gas profile along the vertical axis, from ref. [25]:
left, N_2 and H_2; right, O_2, NO and CH_4.

In the concluding paragraph of the paper, the big difficulty arises in the application of the hard spheres model to the solubility data of gases. The model cannot explain the intriguing result of his (and Henry's) experiments: why different gases dissolve differently in water? It has been suggested [8] that Dalton answered this question by invoking the correlation between solubility and density data.

On September 19th, 1803, the specific gravities of several gases (with respect to air) are reported in the laboratory notebook, including those of the first and last group of the table, i.e., hydrogen (0.077), nitrogen (0.966), *"carbonic acid [CO_2]"* (1.500), *"nitrous oxide [N_2O]"* (1.610). Taking into consideration only the gases on which solubility data were known at the reading date, the indication is clear: elementary and low-density gases are scarcely soluble in water while compound and high-density gases are appreciably soluble. Given this premise, to the question *"why does water not admit its bulk of every kind of gas alike?"* Dalton was enabled to answer with great ingenuity (bolds are our additions) ***"the circumstance depends on the weight and number of the ultimate particles of the several gases**: Those whose particles are lightest and single being least absorbable and the others more according as they increase in weight and complexity"*[31]. Dalton had in mind **weight** and **complexity** of the *"ultimate particles"*, thus initiating the transition from a physical to a chemical atomic theory. The correlation of solubility with density led to a research project described in these terms *"An enquiry into the relative weights of the ultimate particles of bodies is a subject, as far as I know, entirely new: I have lately been prosecuting this enquiry with remarkable success."* Thus, the paper ends with the result of this enquiry, a long table (see **Fig. 5**) containing *"the relative weights of the ultimate particles of gaseous and other bodies"*. How this table was obtained by Dalton and on which criteria was based in order to get to the particles' weights is the subject of the next Section.

TABLE	
of the relative weights of the ultimate particles of gaseous and other bodies.	
Hydrogen	1
Azot	4.2
Carbone	4.3
Ammonia	5.2
Oxygen	5.5
Water	6.5
Phosphorus	7.2
Phosphuretted hydrogen	8.2
Nitrous gas	9.3
Ether	9.6
Gaseous oxide of carbone	9.8
Nitrous oxide	13.7
Sulphur	14.4
Nitric acid	15.2
Sulphuretted hydrogen	15.4
Carbonic acid	15.3
Alcohol	15.1
Sulphureous acid	19.9
Sulphuric acid	25.4
Carburetted hydrogen from stag. water	6.3
Olefiant gas	5.3

Fig. 5 – The table of relative weights of *"ultimate particles"* of elements and compounds from ref. [25].

5 – Dalton's chemical atomism

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[31] Ref. [25], p. 286. In the footnote, Dalton adds: *"Subsequent experience renders this conjecture less probable"*.

In his laboratory notebook, September 6th, 1803, Dalton wrote notes bound to become a milestone in the history of chemistry [4]. The earliest set of *"characters* [chemical symbols]*"* was drawn to represent the *"ultimate particles"* of the elements and to give an unequivocal description of their combination in a compound. In agreement with his idea of atoms, Dalton's *"characters"* are circles with a distinguishable inner part; the initial choice for hydrogen and oxygen (open and dotted circle, respectively) were interchanged in later tables. The original page 244, taken from ref. [4], is shown in **Fig. 6**.
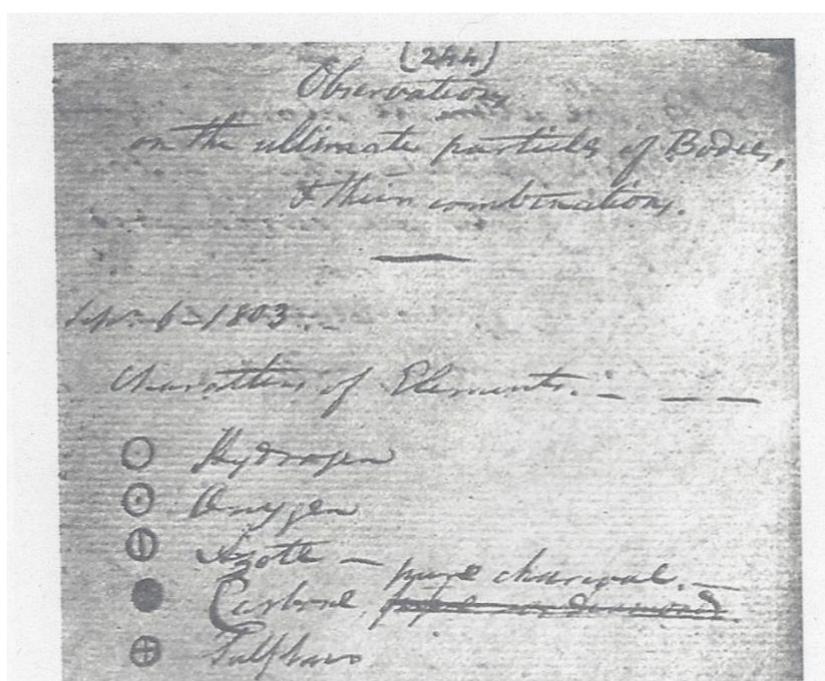

Fig. 6 – First table of *"characters* [symbols]*"* for atoms. It is written:
"244
Observations
on the ultimate particles of bodies
and their combinations
September 6th, 1803
Characters of Elements
   ○   *Hydrogen*
   ⊙   *Oxygen*
   Ⓓ   *Azote*
   ●   *Carbone, pure charcoal*
   ⊕   *Sulphur"*

Page 248, shown in **Fig. 7**, contains the first table of (relative) atomic weights, two years before that of **Fig. 5**. The numerical values could have been easily established from the relative gas densities if Dalton had been willing to accept what is now known as the Avogadro's principle. For instance, from the densities reported in the notebook[32], the oxygen and nitrogen weights would have been found to be 14.6 and 12.5, respectively, that of hydrogen. But this hypothesis was rejected since the very first conception of the atomic theory with the following words

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[32] See ref. [4], p. 41.

"Though it is probable that the specific gravities of different elastic fluids have some relation to that of the ultimate particles, yet it is certain that they are not the same thing; for the ult. part. of water or steam are certainly of greater specific gravity than those of oxygen, yet the last gas is heavier than steam"[33].

It is plain, Dalton says, that, if the *"ultimate particle"* of water is composed by those of oxygen and hydrogen, it must be heavier than that of oxygen. Then, being experimentally observed that the water vapour is less dense than oxygen, this necessarily means that in equal volumes fewer particles of water vapour are contained than of oxygen. This was not a unique example since from the same table (see footnote 32) it is seen that ammonia, formed by nitrogen and hydrogen, is less dense than nitrogen, and carbon oxide, formed by oxygen and carbon, is equally less dense than oxygen. It would be difficult to avoid the conclusion that different numbers of particles were in the same volume of several gases [48].

Fig. 7 – The first table of the relative weights of elements and compounds from the original in ref. [4].
It is written on page 248:

"   Ult. at.   Hydrogen   1

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[33] Ref. [4], p. 27. The rebuttal of Avogadro's hypothesis was justified by Dalton also on a different basis in *A New System of Chemical Philosophy*, p. 71: *"It is evident the number of ultimate particles or molecules in a given weight or volume of one gas is not the same as in another: for, if equal measures of azotic and oxygenous gases were mixed, and could be instantly united chemically, they would form nearly two measures of nitrous gas, having the same weight as the two original measures; but the number of ultimate particle could at most be one half of that before the union. No two elastic fluids, probably, therefore, have the same number of particles, either in the same volume or the same weight"*. The apparently impeccable argument of Dalton runs as follows: starting from n *"ultimate particles"* of nitrogen and n of oxygen in equal volumes V, *"nitrous gas"* is obtained in the volume $2V$. Since the particles of *"nitrous gas"* cannot be more than n, this means that $\frac{n}{2}$ particles of *"nitrous gas"* are in the volume V.

20

-------	*Oxygen*	*5.66*
-------	*Azot*	*4*
-------	*Carbon (charcoal)*	*4.5*
-------	*Water*	*6.66*
-------	*Ammonia*	*5*
-------	*Nitrous gas*	*9.66*
-------	*Nitrous oxide*	*13.66*
-------	*Nitric acid*	*15.32*
-------	*Sulphur*	*17*
-------	*Sulphureous acid*	*22.66*
-------	*Sulphuric acid*	*28.32*
-------	*Carbonic acid*	*15.8*
-------	*Oxide of carbone*	*10.2"*

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Excluding the information from physical data, Dalton made use of chemical data for the derivation of atomic weights. In simple words, the question was: being known from the Lavoisier analysis that the oxygen weight content of water is 85% (and hydrogen 15%), is it possible to determine the weight of an oxygen atom (with respect to hydrogen)? The entries of **Fig. 7** contain the Dalton answer not only for oxygen (5.66) but also for three other elements (nitrogen, carbon, and sulphur, 4, 4.5 and 17, respectively), however without any detailed explanation of the computational procedure to arrive at these values. It has been said [8,18] that all calculations, implicitly or explicitly, are based on the following principles: (i) matter is constituted of extremely minute particles (atoms), (ii) atoms are indivisible and cannot be created or destroyed, (iii) 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 by a fixed number of atoms of its component elements (law of definite proportions) and its weight is the sum of the weights of the constituent atoms, (vi) if more than one compound of two elements is known, the numbers of atoms of either element in the compound particle are in the ratio of whole (small) numbers (law of multiple proportions).

Given a binary compound of A and B composed of particles with n atoms of A and m of B, i.e., $A_n B_m$, and the weight percent, $(\%)_A$ and $(\%)_B$, in the compound, the atomic weight of B with respect to A, $\frac{p_B}{p_A}$, results $\frac{p_B}{p_A} = \frac{n}{m} \cdot \frac{(\%)_B}{(\%)_A}$. To determine $\frac{p_B}{p_A}$, it is then necessary to know not only the percent composition of each element in the compound but also the number of A and B atoms entering the particle. If this latter information is missing but it happens that only one compound of A and B is formed, Dalton adopted the *"rule of greatest simplicity"*; he reasonably assumed that the compound is AB, $n = m = 1$, unless there is some reason to the contrary. The water particle was taken to be OH and therefore $\frac{p_O}{p_H} = \frac{0.85}{0.15} = 5.66$. Being not known any other compound of nitrogen and hydrogen in addition to ammonia, which in an old Austin analysis was reported to be composed by about 80% nitrogen and 20% hydrogen, Dalton found $\frac{p_N}{p_H} = \frac{0.80}{0.20} = 4$ with the ammonia particle expressed as NH. The atomic weight of carbon, $\frac{p_C}{p_H} = 4.5$, was determined from the Lavoisier analysis of the *"carbonic acid"* gas, 72% oxygen and 28% carbon. Since two gases, *"carbonic acid"* and *"oxide of carbone"*, are composed by the same elements, carbon and oxygen, the specification of the *"ultimate particles"* requires an additional proviso. The extended version of the *"rule of greatest simplicity"* dictates that in this case one particle is CO and the other CO_2 or C_2O[34]. Dalton correctly opted for CO_2, as to

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[34]Dalton in later years justified this rule starting from the Newtonian proposition 23 [49] with the following speculation about the atomic architecture of the AB_n particles: *"When an element A has affinity for another, B, I see no mechanical*

21

"carbonic acid", and for CO in the case of *"oxide of carbone"*, using probably as a clue the relative gas densities (see footnote 32). With this assignment he calculated $\frac{p_C}{p_H} = \left(\frac{p_C}{p_O} \cdot \frac{2}{1}\right) \cdot \frac{p_O}{p_H} = \left(\frac{0.28}{0.72} \cdot 2\right) \cdot 5.66 = 4.4$ (in the table of **Fig. 7** the entry 4.5 is either a miscalculation or a "rounded off" value [4]). In the same table the reported weights of the *"ultimate atoms"* of the two gases are 15.8 (CO_2) and 10.2 (CO). As to the atom of sulphur, two sets of data were available for the *"sulphuric acid"* gas, one from Chenevix (61.5% sulphur; 38.5% oxygen) and the other from Thenard (56% sulphur; 44% oxygen). As for the pair CO/CO_2, the particles of *"sulphureous acid"* and *"sulphuric acid"*, not breaking with the *"rule of greatest simplicity"*, were taken to be (incorrectly) SO and SO_2. *"Sulphuric acid"* was assumed to be SO_2, the choice being presumably based again on the densities of the two gases (see footnote 32). The atomic weight of sulfur was calculated from the expression $\frac{p_S}{p_H} = \frac{p_S}{p_O} \cdot \frac{p_O}{p_H}$, which gives 18.1 and 14.4 depending on the set of data, averaged to 17. The weights of SO and SO_2 are 22.66 and 28.32 (see **Fig. 7**)[35].

The last three entries of the table refer to *"nitrous gas"*, *"nitrous oxide"* and *"nitric acid"*. According to the *"rule of greatest simplicity"* and given the relative gas densities (see footnote 32) they were formulated as NO, N_2O and NO_2. The assignment is correct for the first two gases. As to the third, since Dalton accepted the composition proposed by Lavoisier for nitric acid [18], the weight was calculated $4 + 2 \cdot 5.66 = 15.32$, corresponding to NO_2. In addition, since the atomic weight of an element does not vary from a compound to another, as a second point of interest in these gases Dalton observes that *"from the composition of water* [OH] *and ammonia* [NH] *we may deduce ult. at. azot* 1 *to oxygen* 1.42 [i.e., $\frac{p_O}{p_N} = \frac{p_O}{p_H} \cdot \frac{p_H}{p_N} = \frac{5.66}{4} = 1.42$]*"* so that the *"ult. atom of nit. gas* [NO] *should therefore weigh* 2.42 *azot* [i.e., $p_{NO} = 2.42 p_N$]*"*[36]. The law of equivalent proportions says that the ratio r of the weight of oxygen to that of nitrogen in the three oxides is either equal to 1.42 or a simple multiple or fraction of 1.42 (see **Table I**). This means that also the law of equivalent (or reciprocal) proportions is implied by the theory [18]. In occasion of the first lecture, December $22^{nd}, 1803$, of a series of 20 at the Royal Institution in London Dalton received the experimental results of Davy on the three compounds, reported by Dalton in **Table I** [4].

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reason why it should not take as many atoms of B as are presented to it, and can possibly come into contact with it (which may probably be 12 *in general),* <u>except so far as the repulsion of the atoms of B among themselves are more than a match for the attraction of an atom of A.</u> *Now this repulsion begins with* 2 *atoms of B to one of A, in which case the two atoms of B are diametrically opposed; it increases with* 3 *atoms of B to* 1 *of A, in which case the atoms of B are only* 120° *asunder; with* 4 *atoms of B it is still greater, as the distance is then only* 90°*; and so on in proportion to the number of atoms. It is evident then from these positions that, as far as powers of attraction and repulsion are concerned (and we know of no other in chemistry) ……* <u>binary</u> *compounds must first be formed in the ordinary course of things, then* <u>ternary</u> *and so on, till the repulsion of the atoms of B …… refuse to admit any more"*.

[35]It should be again stressed that the relative atomic weights could have been determined from the weight percent and the Avogadro principle. In fact, being in this hypothesis $m\frac{p_B}{p_A} = (\%)_B \cdot \frac{(np_A + mp_B)}{p_A} = (\%)_B \cdot \frac{\rho(A_nB_m)}{\rho(A)}$, the weight of B in A_nB_m results to be an integral multiple of $\frac{p_B}{p_A}$. Thus, analyzing a sufficiently large group of compounds of B and determining their densities $\rho(A_nB_m)$ (together with $\rho(A)$, the A density) at equal temperature and pressure, the smallest of these multiples corresponds very probably to $m = 1$ and therefore identifies $\frac{p_B}{p_A}$. This proposal, which is substantially the Cannizzaro rule, was unfortunately advanced only sixty years later.

[36] Ref. [4], p. 28.

Table I – The composition of the three nitrogen oxides according to theoretical (Dalton) and experimental (Davy) results. The particle weight is expressed in units of the nitrogen weight (see ref. [4]); r is the ratio $\frac{O(\%)}{N(\%)}$.

	weight	Dalton results				Davy experimental results			
		N(%)	O(%)	r		N(%)	O(%)	r	
N$_2$O	2+1.42	58.5	41.5	0.71	0.5	63.3	36.7	0.58	0.46
NO	1+1.42	41.3	58.7	1.42	1	44.05	55.95	1.27	1
NO$_2$	1+2·1.42	26.0	74.0	2.84	2	29.5	70.5	2.39	1.88

Within approximately one month from September 6th Dalton (i) tested the theory regarding the dependence of the gaseous solubilities on the particle weight and (ii) presented a set of chemical formulae for an appreciable number of compounds. On September 19th, 1803, eleven gases were arranged in order of increasing weight and divided into three groups [4] (see **Fig. 8**). Hydrogen and nitrogen, having the least particle weights, are the least soluble gases in water. On the opposite, *"nitrous oxide* [N_2O]*"*, *"sulphurated hyd. gas* [H_2S]*"* and *"carbonic acid gas"* with the highest particle weight are the most soluble gases. In the middle six gases of intermediate weights have intermediate solubilities. Once compared with the second *"article"* of the paper [18], the order results being nearly the same, except for CO.

Fig. 8 – The three groups of gaseous solubilities ordered according to the weight of the compound atom. The *"carbonated hyd. gas"* is ethylene, elsewhere called *"olefiant gas"*, while the *"carb. aqueous vapour"* was later shown by Dalton to be a mixture of CO and H_2.

The table of **Fig. 8** was probably prepared to establish the correlation between solubilities and diameters of gaseous particles [8]. Dalton calculated this parameter (with respect to the diameter of a reference particle, in this case that of liquid water, see footnote 32) assuming that the gas is an ordered array of spherical particles. The attempt was obviously unsuccessful, and the negative result may have caused the appearance of the already cited footnote in the paper of 1805 [25] about the lower probability of the atomic *"conjecture"*.

On October $12^{th}, 1803$, a classified list of *"ultimate atoms"* of compounds appears in the notebook, reproduced in **Fig. 9**. The advantages of the Dalton approach to identify the compound are apparent, (i) each atom has its own symbol, (ii) the compound particle is represented by means of the symbols of the constituting elements and (iii) the number of times each atom is present in the compound particle is indicated by the symbol repetition. In **Fig. 9** the phosphorus symbol is added to those of nitrogen, sulphur, hydrogen, and oxygen (the latter two are exchanged with respect to **Fig. 6**). Dalton distinguishes binary, ternary, etc. *"ultimate atoms"*, some of which have been already considered in the table of **Fig. 7**. Among binary particles, *"carbonated hydrogen gas* [i.e., *"olefiant gas"*, ethylene]*"* is formulated as CH, *"phosphorous acid"* as PO and *"phosphorated hydrogen* [posphine]*"* as PH. *"Ether"* is constituted by ternary particles C_2O. In analogy with *"sulphuric acid"*, the formula of *"phosphoric acid"* is PO_2[37]. Tetra- and penta-atomic particles are viewed as second-order compounds. Thus, alcohol is $CH + OH$, the combination of the hydrocarbon particle CH with water OH. Sugar is $CO + OH$, *"gaseous oxide of carbon* [CO]*"* and water OH. In *"nitrous acid* [N_2O_3]*"* the complicated ratio $2:3$ is expressed as the combination of two particles, $NO + NO_2$ [18].

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[37] The atomic weight of phosphorus, $\frac{p_P}{p_H} = 7.2$, appears in the notes of September $19^{th}, 1803$ [4] and is calculated considering the Lavoisier data about *"phosphoric acid* [PO_2]*"*, 39.4% phosphorus and 60.6% oxygen, and assuming 5.5 as the atomic weight of oxygen.
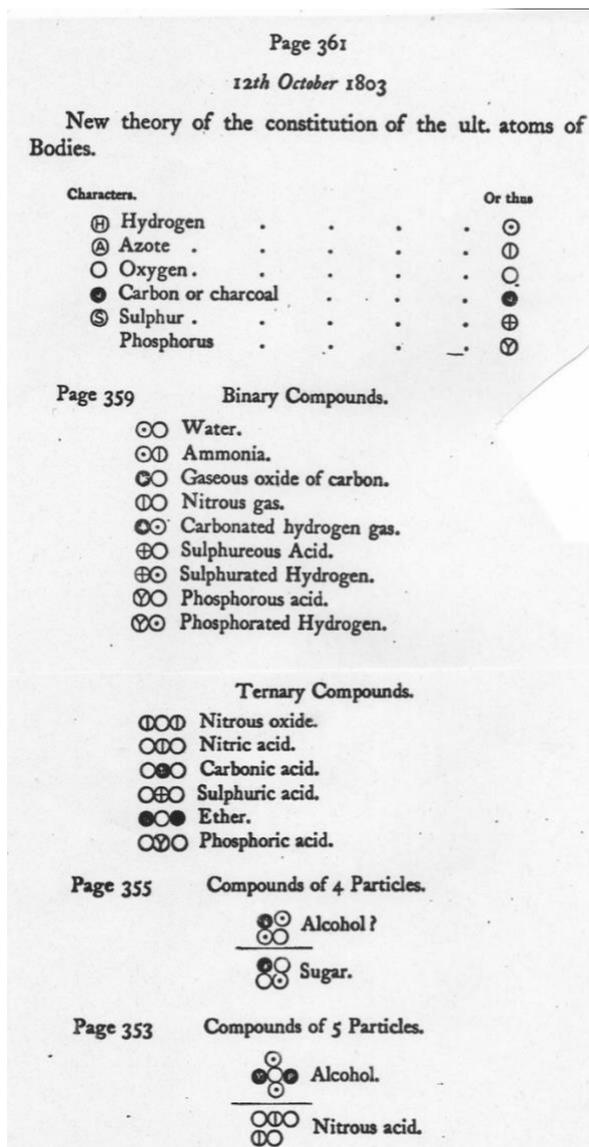
Fig. 9 – The constitution of some bi- and polyatomic particles according to the Dalton theory.

The notes contained in the Dalton's notebook between September and October 1803 are the essence of the chemical atomic theory. The theoretical principles remained unchanged in all later publications [5,18]. Comparing now with the table of **Fig. 5**, the gases present in **Fig. 7** and **9** appear in this table with compositions confirmed except in two cases. The *"ether"* particle is represented as C_2H in **Fig. 5**, not C_2O, with weight $2 \cdot 4.3 + 1 = 9.6$ and the particle of alcohol as C_2OH (not COH_2) with weight $2 \cdot 4.3 + 5.5 + 1 = 15.1$. But a new piece of information appears in **Fig. 5** and comes from the *"carburetted hydrogen from stagn. water* [methane]*"* formulated as CH_2 with weight $4.32 + 2 = 6.3$. As already noted, the relation between methane and ethylene (*"olefiant gas"*) was established almost one year after the proposal about the atomic theory. Dalton describes in his notebook, August 24th, 1804, the reaction of ethylene and methane with oxygen with volumetric details [4]

<table>
<tr><td></td><td colspan="3">*"Olefiant gas* [ethylene]</td></tr>
<tr><td>*Meas.*</td><td>*Acid.*</td><td>*Oxy.*</td><td>*Dimin.*</td></tr>
<tr><td>100</td><td>200</td><td>300</td><td>200</td></tr>
<tr><td></td><td colspan="3">*Stagnant* [methane]</td></tr>
<tr><td>100</td><td>100</td><td>200</td><td>200*"*[38]</td></tr>
</table>

which may be interpreted in modern terms as

$$C_2H_4 + 3O_2 \rightarrow 2CO_2 + 2H_2O$$

$$CH_4 + 2O_2 \rightarrow CO_2 + 2H_2O$$
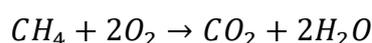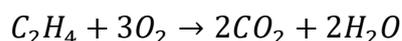
Fixing the same number of carbon atoms for both compounds, i.e., the same volume of *"carbonic acid"* gas precipitated by *"water lime"*, for instance 100 *"measures"*, a little reflection on the volumetric data shows that the volumes of the reacting and products gases (in the same order given by Dalton) are in the ratio $50 : 100 : 150 : 100$ for ethylene and $100 : 100 : 200 : 200$ for methane. Thus, the final volumes in the fourth place are $1 : 2$ and therefore the ratio of the hydrogen atoms in the particles of the two gases is $1 : 2$. This means that the particle of *"carburetted hydrogen from stagn. water"* contains a number of hydrogen atoms double that in *"olefiant gas"*. The former was formulated as CH_2 and the latter as CH, a conclusion which stands as the first successful experimental verification of the atomic theory after one year of silence [8]. It was a result particularly impressive for Dalton to the point that he informed Thomson, who visited him August 27th, 1804, about the atomic theory referring specifically to these gases. This narrative, centered on the chemical development of the theory one year later with respect to the intimation, has been questioned and it was argued, on the contrary, that Dalton actively tested the implications of the incipient theory from the start and was eager to communicate his merits [10]. For instance, it has been noted [10] that the law of multiple proportions was already in operation in the table of **Fig. 7** and considered as the rule by means of which the atom-to-atom association in the compound formation may occur. Examples are the weights of the *"ultimate atoms"* of the oxides of nitrogen, carbon and sulfur [10]. As to the diffusion of the theory, Dalton included the atomic theory as a small part of the subject matter in the lectures held at the Royal Institution on natural philosophy in the period December 1803 – January 1804, as evidenced by reported annotations [10]. In this occasion Dalton was introduced to Davy and not only was informed about nitrogen oxides but also, had the opportunity to present to Davy the atomic theory. Finally, on his return to Manchester Dalton gave on February lectures whose content is unfortunately not known but whose titles suggest that atomic theory was part of them [10].

6 – Conclusions

In this paper, the attention is directed to the history of Dalton scientific interests from the studies in meteorology to the first intimation of the chemical atomic theory. The distinctive traits of his personality were great perseverance, self-reliance, and a laborious mind. He promoted vigorously the theory of mixed gases explaining atmospheric homogeneity in terms of repulsive forces acting among

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[38] Ref. [4], p. 63.

particles of the same kind rather than of affinity or chemical combination. Differing specific gravities of the particles would have caused the atmospheric gases to settle down in layers. To avoid this difficulty Dalton opted for the theory of mixed gases which would ultimately lead to the formulation of the atomic theory. But he had a peculiar aversion to the idea of a direct relation between specific gravities and particle weights. The statement was reiterated over the years saying that it is a *"confused idea …… that the particles of elastic fluids are all of the same size"*[39].

Dalton's contributions to the atomic theory have been discussed at length [9,47]. There is no need to say that the idea dates back to the Greek (and earlier) philosophies and that interest in the atomic theory revived in the XVII century [7,17,19]. The following magnificent, perhaps unsurpassed, passage of Newton's *Opticks*, transcribed by Dalton's own hand in the notebook [4,48], is proof that atomistic ideas were diffused among the XVIII century scientists

"All these things being consider'd, it seems probable to me, that God in the Beginning form'd Matter in solid, massy, hard, impenetrable Particles, of such Sizes and Figures, and with such other Properties, and in such Proportion to Space, as most conduced to the End for which he form'd them; and that these primitive Particles being Solids, are incomparably harder than any porous Bodies compounded of them; even so very hard, as never to wear or break in pieces; no ordinary Power being able to divide what God himself made one in the first Creation. While the Particles continue entire, they may compose Bodies of one and the same Nature and Texture in all Ages: But should they wear away, or break in pieces, the Nature of Things depending on them, would be changed. Water and Earth, composed of old worn Particles and Fragments of Particles, would not be of the same Nature and Texture now, with Water and Earth composed of entire Particles in the Beginning. And therefore, that Nature may be lasting, the Changes of corporeal Things are to be placed only in the various Separations and new Associations and Motions of these permanent Particles; compound Bodies being apt to break, not in the midst of solid Particles, but where those Particles are laid together, and only touch in a few Points."

Thus, the striking advance of Dalton's theory may be synthesized in three points, (i) the emphasis on a single atomic property, the weight of the atom, singled out of the several properties of the *"ultimate particles"* envisioned by Newton, weight (*"massy"*), hardness (*"hard"*), size, shape (*"figures"*) [8], (ii) the calculation procedure for deriving atomic weights or, in other words, the rule of greatest simplicity [9,10], (iii) the symbolic representation of atoms and their combinations [4].

Acknowledgements

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