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The Reinvention of the Nitrous Gas Eudiometrical Test in the Context of Dalton's Law on the Multiple Proportions of Combination

Pere Grapí

Societat Catalana de Química
E-mail: *pgrapi@gmail.com*

Abstract. Dalton's chemical atomism was inspired by his physical fascination with gases and developed through his chemical investigation. In regard to the latter, Dalton's very first chemical experiments on nitrogen oxides enabled him to identify the first verifiable case of multiple proportions of combination, as well as playing a significant role in the process of establishing the basis for the reinvention of the nitrous gas eudiometer. Nevertheless, the eudiometrical background of Dalton's trials on the oxides of nitrogen is yet to be elucidated. His interest in the nitrous gas test was in principle concerned with the justification of his statement on the multiple combining proportions, rather than with the improvement of the test as a eudiometrical method for verifying the oxygen content in common air. On the whole, after passing through Dalton's hands, the nitrous gas test was returned to eudiometrists as a simpler type of the eudiometrical test than those performed with the latest nitrous gas eudiometers. In 1809, in line with Dalton's suggestions, Gay-Lussac was eventually able to deliver a reshaped version of the nitrous gas eudiometer.

Keywords. Nitrous gas test, Dalton, eudiometry, proportions of combination, Gay-Lussac.

AN OVERVIEW OF THE NITROUS GAS TEST

In a landmark paper, *Observations on Different Kind of Airs*, read in 1772 but published in the following year, Joseph Priestley (1733-1804) proposed a nitrous air (nitrogen monoxide) test to replace the use of mice and birds for checking the goodness (i.e. the respirability) of an air sample.[1] For this test, Priestley was indebted to Stephen Hales' (1677–1761) work *Statical Essays* of 1738.[2] Nevertheless, the chemical phenomenon underpinning the test had already been observed by John Mayow (1640-1679) in 1674, and described by Hales himself in his previous work *Vegetable Staticks* of 1727.[3] The purpose of this development was not only to achieve a greater precision, but also to remove the inconvenience of maintaining a stock of mice in the appropriate conditions.[4] This nitrous air test relied on the contraction in volume that an air sample underwent when mixed with nitrous air.[5]

The relevant reactions taking place in the nitrous air test carried out over water are equilibrium processes that do not occur independently. They are outlined in the following chemical equations:

$2\ NO\ (g) + 2\ O_2\ (g) = 2\ NO_2\ (g)$	Relatively slow and proceeds essentially to completion within minutes.
$2\ NO_2\ (g) = N_2O_4\ (g)$	Rapidly achieve equilibrium.
$NO\ (g) + NO_2\ (g) = 2\ N_2O_3\ (g)$	Rapidly achieve equilibrium.
$N_2O_4\ (g) + H_2O\ (l) = HNO_3\ (aq) + HNO_2\ (aq)$	Fast and irreversible.
$N_2O_3\ (g) + H_2O\ (l) = 2\ HNO_2\ (aq)$	Fast and irreversible.

Additionally, oxygen dissolved in the water can play a role.

The goodness of air was considered to be inversely proportional to the content of phlogiston. Priestley was of the opinion that nitrous air appeared to consist of the nitrous acid vapour combined with an excess of phlogiston. On mixing nitrous and common air, this nitrous acid vapour disengaged from the phlogiston, which united with the acid principle of the common air, while a fixed air that it contained was precipitated out, and the water in which the mixture was made absorbed the acid of the nitrous air. These two latter phenomena caused the contraction in volume of the air mixture.[6]

Indeed, during the last quarter of the eighteenth century, doubts began to be cast on the simple nature of atmospheric air, and the idea that only a part of the common air was breathable started to gain acceptance. Then, in parallel with the hygienist approach to atmospheric air, a more analytical and quantitative methodology to determine the composition of common air was adopted, mainly in regard to the uncertainty about its proportion of respirable or vital air; that is, our oxygen.

Priestley presented the experimental device he conceived for conducting the nitrous air test in the first and second volumes of his work *Experiments and Observations on Different Kinds of Air* (1774-1775, 1776).[7] This experimental device was very simple. It consisted of collecting the common air measures by means of a number of vials of proportional capacities (Figure 1: f, f, f), and a cylindrical tube (g) on which all these measures were engraved in order to indicate where to mix the common and nitrous air.

This experimental device was to become a source of inspiration for investigators such as Marsilio Landriani (1751-1815), Felice Fontana (1730-1805) and, in particular, Jan Ingenhousz (1730-1799). Priestley did not christen his experimental device with any particular name, and it was Landriani who in 1775 coined the term "eudiometer" for his own instrumentalist version of the nitrous air test (Figure 2).[8] Hereafter I will refer to this test as the "nitrous gas test".

From 1778 onwards, the nitrous gas eudiometers had to coexist with different kinds of eudiometers. As experimental devices, all eudiometers were based on the fact that the respirable part of atmospheric air could be extracted from an air sample by the action of a particular substance. These absorbent substances could be solid materials (phosphorus, iron filings with sulphur and potassium sulphide), aqueous solutions (iron sulphate

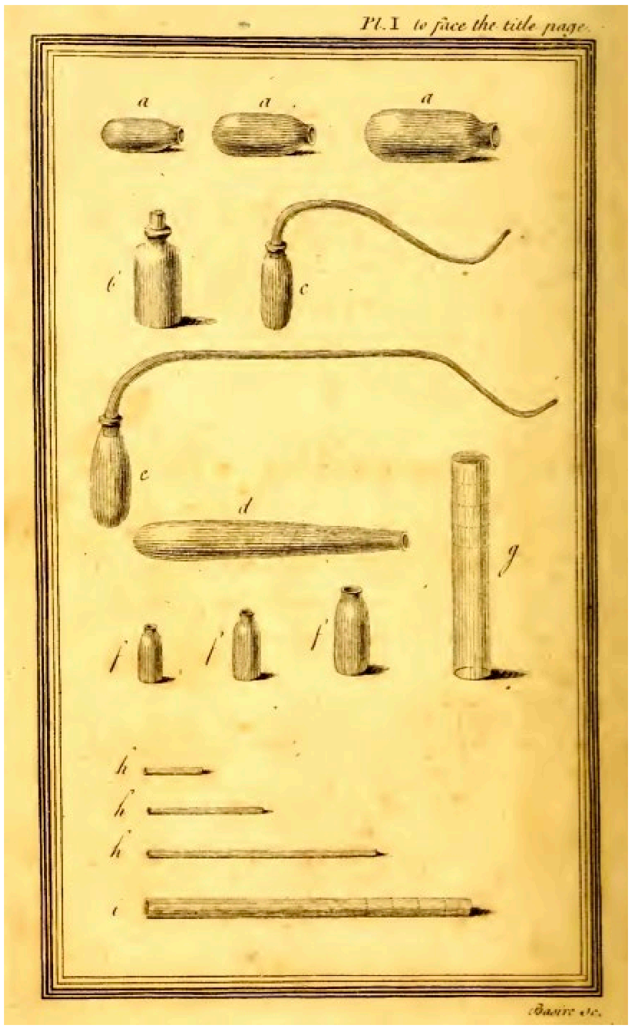

Figure 1. Priestley's glass vials used for eudiometrical measurements. From Joseph Priestley, *Experiments and Observations of Different Kinds of Air* (London, 1776), plate I

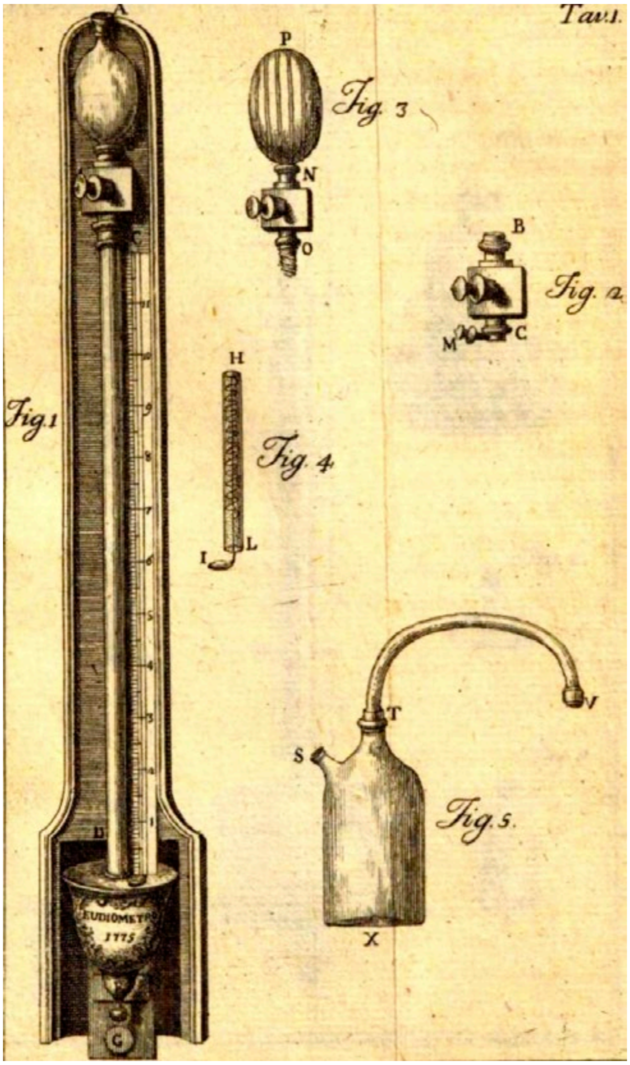

Figure 2. Landriani's eudiometer. From Marsilio Landriani, *Ricerche fisiche intorno alla salubrità dell'aria* (Milano, 1775), plate 1.

impregnated with nitrous gas and alkaline or calcium sulphides) and gaseous substances such as nitrous gas (nitrogen monoxide) and hydrogen, this latter being the basis of Volta's eudiometer (Figure 3).[9] The existence of these competing eudiometers and the difficulties surrounding the procedural standardisation of the nitrous gas eudiometer eclipsed its utility.[10] Nevertheless, the nitrous gas test was far from being dismissed and would mutate into a new version at the beginning of the nineteenth century.

After this overview of the nitrous gas test, it is time to examine John Dalton's involvement in this eudiometrical test.

JOHN DALTON (1766-1844). LAYING THE FOUNDATIONS FOR THE RECONVERSION OF THE NITROUS GAS TEST

The first public description of Dalton's experiments on nitrogen oxides appeared in his paper *Experimental Enquiry into the Proportions of the Several Gases or Elastic Fluids Constituting the Atmosphere*, read on November 12th, 1802, at the Literary and Philosophical Society of Manchester, and which remained unpublished until 1805. Dalton's account of his experiments is commonly regarded as the confirmation of his understanding of multiple proportions in the nitrogen oxides.

Unfortunately, Dalton's notebook, together with many of his papers held in Manchester, were destroyed as the result of an air raid in 1940 during the Second World War. The only surviving references to the notebook are to be found in the work by Roscoe and Harden, *A New View of the Origin of Dalton's Atomic Theory*. In a discussion of Dalton's experimental results on nitrogen oxides, these authors state that the interesting question was not *how* Dalton managed to obtain them, but *when* he obtained them.[11] The chronology of these experiments undoubtedly constitutes a crucial part of the origin and development of Dalton's widely studied chemical atomic theory.[12] Even so, a knowledge of *how* these experimental results were obtained would enable both they and the origin of the atomic theory to be placed in their instrumental and procedural context.

Dalton gave an account of the first clear instance of multiple proportions of combination in the first section of his 1805 paper. This section, entitled *Of the Weight of the Oxygenous and Azotic Atmospheres*, was devoted to assessing different eudiometrical procedures in relation to the composition of common air. Although Dalton had had the opportunity, prior publication, to revise the draft of this paper, which he read in 1802, the eudiometrical context of his early experiments on the oxides of nitrogen nevertheless remained unclear.[13] Notwithstanding, there is no doubt that in the published and debatable version of his 1805 paper, Dalton wished to frame these experiments in a eudiometrical context.

A beginner in chemistry and eudiometry

In order to gain an understanding of Dalton's knowledge in the field of eudiometry, it would first be worthwhile to become acquainted with the extent of his training in chemistry before 1805. During his stay in Kendall (1781-1793), his post as an assistant teacher at a boarding school provided him with access to the vast library of his tutor and friend, the natural philoso-

Figure 3. (Left) A view of the lower part of a copy of the Volta-type eudiometer. (Right) Modern replica of Spallanzani's phosphorus eudiometer exhibited at the Centro Studi Lazzaro Spallanzani. Courtesy of Tempio Voltiano, Musei Civici di Como, Comune di Como and of Centro Studi Lazzaro Spallanzani, Scandiano, photography by the author.

pher John Gough (1757-1825), as well as to the impressive library at the school, where he became familiar with Boyle's and Boerhaave's works. In 1793, he moved to Manchester to teach mathematics and natural philosophy at the New College, but soon found himself obliged to teach chemistry as well. While in Manchester he entered a more challenging scientific world than the one he had known in Kendall, and in 1794 went on to become an elected member of the Manchester Literary and Philosophical Society, of which he became Secretary in 1800 and President in 1817. Dalton's involvement in the activities of this Society and his close friendship with William Henry (1774-1836) considerably extended his scientific knowledge and experience.

It was in Manchester, in early 1796, where Dalton received his first formal education in chemistry thanks to a series of thirty chemical lectures given by Thomas Garnet (1776-1802), who was to become a professor at the Royal Institution in London. After these lectures he felt confident enough in his expertise in chemistry to agree to give some six lectures on chemistry the following summer in Kendall. In 1800, he resigned his teaching position and opened his own Mathematical Academy, where he offered tuition in mathematics, experimental philosophy and chemistry. In March 1803, he informed his brother that in his leisure time he had been very busily engaged in his chemical and philosophical enquiries.[14] It would not be presumptuous to say that prior to 1805 Dalton had had access to the foremost chemistry books and scientific journals, first, in Kendall, in Gough's private library, and then in Manchester in the extensive Chetham's Library as well as in the Society's library, not to mention his own private library.[15]

There exists no published trace of Dalton's involvement in eudiometrical tests before the publication of his 1805 paper on the proportions of the several atmospheric gases. Nevertheless, it seems that Dalton was well acquainted with the current eudiometrical methods after attending the chemical lectures in 1796. Thus, in the sequel to a paper on the constitution of the atmosphere, published in 1837, Dalton affirmed that he had been engaged in the investigation of the proportions of oxygen and nitrogen in mixtures of both gases for more than forty years.[16]

The eudiometrical context of Dalton's law of multiple proportions

Dalton began the first section of this 1805 paper by listing the five eudiometrical tests widely used at that time: nitrous gas, alkaline or calcium sulphides, hydrogen ignition, green sulphate or chloride of iron impregnated with nitrous gas, and phosphorous fast combustion. He then made it clear that he regarded the finding that atmospheric air contained 21% oxygen as an accepted fact, explaining past discrepancies as a misunderstanding of the nature of the different tests and of the circumstances influencing them.

It was nothing unusual for Dalton to focus his attention in the nitrous gas test, given his work on meteorology and mixed gases. While he acknowledged the discredit attaching to the nitrous gas test, he valued it for being not only the most elegant and expeditious of all the existing eudiometrical tests, but also as accurate as any other when properly conducted. It appears that Dalton had not been fully aware that the reliability of the test depended on skilful trained experimenters to conduct it. His intimate friend William Henry had discarded it because the sources of error inherent in the employment of the test had caused him to mistrust the results obtained thereby. Henry's reference to Humboldt's researches on the nitrous gas published in the *Annales de chimie* may have influenced Dalton's experimental design and textual presentation of his enquiries into the combination of nitrous gas with atmospheric oxygen. Humboldt's researches proved useful for demonstrating that the test should be performed over water instead of mercury, as well as the influence on the experimental outcomes of the size of the eudiometrical recipient and the order in which gases were added to it.[17] Dalton began his conclusions by criticising the nitrous gas test in four comments mainly regarding some material and procedural aspects of the test already addressed by Humboldt in his paper:[18]

> *I shall, on this occasion, animadvert upon it [the nitrous gas test]*

In his first comment, Dalton pointed out the need of using nitrous gas that was virtually free of azotic gas (nitrogen), with less than 2-3% at most, and nitrous oxide (dinitrogen monoxide). The remaining comments were devoted to summarising his experiments in the form of two eudiometrical trials.

> *The first trial consisted of adding 100 measures of common air to 36 of nitrous gas (NO in Dalton's terms) in a tube 3 $^1/_{10}$ inches wide and 5 inches long. After waiting for a few minutes, the whole mixture was reduced to 79 or 80 measures, without exhibiting signs of either oxygen or nitrous gas. In the second trial, 100 measures of common air were added to 72 of nitrous gas (twice as many in the first trial) in a wide vessel over water so as to form a thin stratum of air.[19] After an immediate momentary shaking, as before, a residue of 79 or 80 measures of pure azotic gas was found. Finally, if fewer than 72 measures of nitrous gas had been used, there would have been a residue containing oxygen, but if more, then some residual nitrous gas would have been found.*

At this point, all the foregoing findings led Dalton to state what has been regarded as a key step in the development of his atomistic reasoning; the discovery of multiple combining proportions:[20]

> *The elements of oxygen may combine with a certain portion of nitrous gas, or with twice that portion, but with no intermediate quantity*

In order to account for the diversity of the results obtained with the nitrous gas test, Dalton suggested that nitric acid (NO_2 in Dalton's terms) had been formed in the first trial, and in the second nitrous acid (N_2O_3 in Dalton's terms).[21] However, since both acids could be formed at the same time, one part of the oxygen went to one of nitrous gas, while another part of oxygen went to two others of nitrous gas.[22] Therefore, the quantity of nitrous gas absorbed had to be variable across a range of 36 to 72 parts for 100 parts of common air. Regarding the size of the tube used, he concluded that the wider the tube the quicker the test could be completed, and the more the mixture was exposed to water the greater was the quantity of nitrous acid and the lesser of nitric acid yielded.

Sometime between October and November, 1803, Dalton carried out a series of experiments on the oxides of nitrogen that he reported in the two trials in his paper of 1805. According to Dalton's notebook, nitrous gas and common air should be suddenly mixed in the second trial.[23] In earlier trials, Dalton had calculated the corresponding nitrous gas–oxygen ratio. Actually, this ratio was nothing but the proportion between nitrous gas and oxygen at the point of saturation.

As far as eudiometrical purposes were concerned, Dalton recommended attempting to form either nitric acid (first trial) or nitrous acid (second trial) entirely alone rather than a mixture of both. However, he decided on the first experiment because it appeared to be the most easily and accurately performed. To this end, he recommended the use of a narrow tube, but wide enough to allow nitrous gas to be absorbed by water without the need for any shaking.[24]

> *The test was executed by providing a little more nitrous gas to the oxygen gas than was sufficient to form nitric acid. As soon as the diminution in volume appeared to be complete, the gaseous residue was transferred to another tube. 7/19 of the loss was due to oxygen.[25] This was necessary to prevent the nitric acid, formed and combined with water, from absorbing the remainder of the nitrous gas to form nitrous acid.*

On October 21st, 1803, nearly a year after the reading of the 1802 paper, Dalton read a paper at the Literary and Philosophical Society of Manchester *On the Absorp-*

tion of Gases by Water and Another Liquids, which also remained unpublished until 1805 in the Memoirs of the Society. By that date, therefore, Dalton had already arrived at the conclusion that the rapid mixture of oxygen and nitrous gas over a broad surface of water occasioned a greater diminution in volume than otherwise.[26]

From 1806 onwards, more details emerged about the development of Dalton's nitrous test thanks to the new editions of William Henry's work *An Epitome of Chemistry*. A personal communication to Henry provides the conclusions of Dalton's study regarding the influence of the size of the tube and the manner in which the gases were mixed on determining the proportion of oxygen in an air sample.

> *If pure nitrous gas was admitted to pure oxygen gas in a narrow tube so that the oxygen gas was uppermost, the two gases united very nearly in the proportion 1.7 [First trial]. If, on the other hand, the nitrous was the upper gas, a much smaller quantity of it disappeared [1 oxygen/1.24 nitrous gas]. If nitrous gas was admitted to pure oxygen gas in a wide vessel over water, the whole effect took place immediately and one measure of oxygen united with 3.4 of nitrous gas [Second trial]. To render this rule more intelligible, Dalton gave as an example the case of 100 measures of common air that were delivered to 100 measures of a mixture of nitrous gas with an equal proportion of azotic or hydrogen gas, which after standing for a few minutes in the eudiometer were found to give 144 measures. When this loss of 56 was divided by 2.7, it gave a measure of almost 21 for the oxygen gas present in 100 measures of common air.*[27]

When analysing atmospheric air samples, it was scarcely necessary to dilute the nitrous gas with any other gas prior to its use. The recommendation was to wait for a certain period of time - 10 minutes, for instance - before noting the diminution in volume, without the need to transfer the residue to another vessel. If the gas sample under examination contained much more oxygen than in atmospheric air, then it was appropriate to dilute the nitrous gas with an equal volume of hydrogen, in which case the narrower the tube the more accurate would be the result.

As regards the experimental equipment, two graduated tubes with funnel-shaped extremities (Figure 4: **1** and **2**) were employed, each from 3 to 4 tenths of an inch in diameter and 8 or 9 inches long.[28]

By 1806, Henry had changed his mind about the employment of nitrous gas for determining the purity of air. He came to prefer Dalton's method to all the others because of its facility, quickness and accuracy, at least for gaseous mixtures of a very similar standard to the atmosphere. Notwithstanding this constraint, the method was valued because it could be applied to determining the proportion of oxygen in some gaseous mixtures to which other eudiometrical tests were not applicable, such as mixtures of hydrocarbons and oxygen gases. The application of nitrous gas to eudiometrical purposes would still admit of further accuracy when used by Gay-Lussac.[29]

GAY-LUSSAC'S STUDY ON THE OXIDES OF NITROGEN. RESHAPING THE NITROUS GAS EUDIOMETER

The combinations of nitrous gas with oxygen constituted one of the issues in chemistry about which little agreement existed at the beginning of the nineteenth century. On March 13th, 1809, Gay-Lussac read the *Mémoire sur la vapeur nitreuse et sur le gaz nitreux considére comme moyen eudiométrique* at the Institut de France, where he reported on his research work, the aim of which was not only to establish the theory of the formation of nitrous and nitric acids using nitrous gas and oxygen, but also the transformation of the nitrous gas eudiometer into an instrument of accuracy.

Joseph-Louis Gay-Lussac (1778-1850) had been appointed to the post of demonstrator (*répétiteur*) at the École Polytechnique in September 1804. He had attended the chemistry lectures given at this same institution by Antoine-François Fourcroy (1735-1809) and Louis-

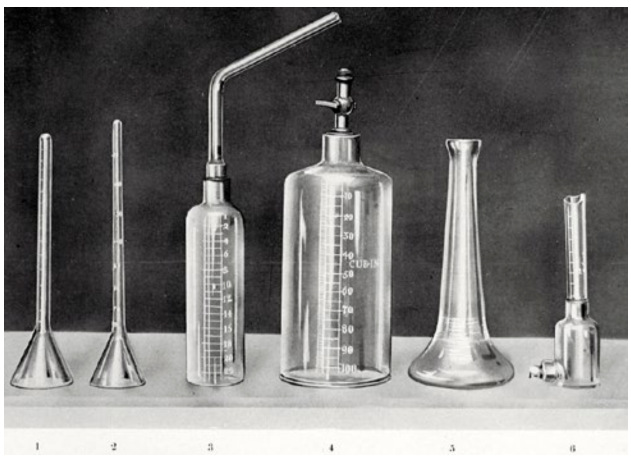

Figure 4. Apparatus that belonged to Dalton.[29] **1**, **2**. Glass funnels with long graduated stems closed at the ends used by Dalton as eudiometrical tubes. **3**. Graduated bell jar with bent tube attached for collecting and measuring gases. **4**. Graduated bell jar with brass cap and stopcock for measuring gases. **5**. Conical glass vessel containing mercury. **6**. A fragment of Hope's eudiometer. From *Memoirs and Proceedings of the Manchester Literary & Philosophical Society*, 1904, Vol. 48 (No. 22), plate 2.

Nicolas Vauquelin (1763-1829) in the first year, by Jean-Antoine Chaptal (1756-1832) in the second year, and by Louis-Bernard Guyton de Morveau (1737-1816) and Claude-Louis Berthollet (1748-1822) in the final year. All were luminaries of French chemistry in the late eighteenth century. Gay-Lussac had the good fortune to be recruited for the Arcueil group by Berthollet, who eventually became the supervisor of his scientific career. His volumetric approach to matter, i.e. his concern with gases, volatile liquids and volumes rather than condensed matter and weights, was largely due to the influence of Berthollet and Pierre-Simon Laplace (1749-1827), the patrons of the Arcueil group.[30]

In his landmark paper of 1808 on the law of combining volumes of gases, Gay-Lussac had ascertained that the nitrous gas (nitrogen monoxide) was composed of equal parts in volume of oxygen and nitrogen.[31] In other words, 100 parts of oxygen and 100 of nitrogen produced 200 parts of nitrous gas without any diminution in volume. He also recalled that nitric acid (dinitrogen pentoxide) was composed of 100 parts of nitrogen and 200 of oxygen. Nitric acid could therefore be regarded as composed of 100 parts of oxygen and 200 of nitrous gas, because the latter contained as much oxygen as nitrogen without any diminution in volume. He also found that 100 parts of nitrogen required 50 parts of oxygen to form nitrous oxide (dinitrogen monoxide).

To obtain the nitric or the nitrous (nitrogen dioxide) acids by combining nitrous gas with oxygen was not simply a matter of first introducing one gas and then the other, but of which gas predominated in the mixture. When oxygen and nitrous gas were mixed in the appropriate ratios, the absorption of the vapour formed thereby was prompt and complete. Thus, by using a narrow tube, nitric acid containing 100 parts of oxygen and 200 of nitrous gas was obtained. However, when both gases were mixed in a slightly larger tube, absorption did not vary significantly, providing that no shaking took place, because water would dissolve the nitrous gas. In this case, the acid obtained was nitrous acid gas. On the other hand, if either of the two gases predominated to excess, the nitrous gas was prevented from coming into contact with the water and dissolving easily. Thus, with an excessive amount of oxygen, nitric acid was produced, while on the other hand an excessive amount of nitrous gas produced nitrous acid.[32]

Despite the discrepancy between Gay-Lussac's results and Dalton's on the composition of the oxides of nitrogen,[33] he did not refrain from stating his conclusions on the influence of the size of the tube in which the gases combined - a key factor in the design of his eudiometrical device. Gay-Lussac's volumetric approach to matter was not the only influence of his mentor Berthollet, whose experience with procedures in large scale chemical productions was probably decisive for his view that chemical phenomena were to a large extent conditioned by their surrounding circumstances. From this perspective, the fact that Gay-Lussac gave so much importance to the size of the reaction tube and its effect on the outcome of the combination of gases may be better understood.

Since the aim of eudiometrical analysis was to remove all the oxygen in an air sample, an excess of nitrous gas was needed in order to obtain a volume reduction four times larger than the volume of oxygen in the sample. Thus, possible errors corresponded to only a quarter of the oxygen, and since it was not possible to err by four degrees, the oxygen content in a gas mixture could be estimated by much less than one-hundredth. The only precautions to be taken were to avoid shaking the mixture and to ensure that nitrous gas was always predominant without too much excess, since the more it was absorbed the less it would be mixed. Even in this case, however, error would never reach a hundredth part of oxygen. In addition to these precautions, two sources of error also had to be taken into account. First of all, if the gases were mixed in a very narrow tube, nitrous acid would scarcely be absorbed by water because of the lack of contact, which would necessitate shaking, in which case nitrous gas would also be absorbed. It was for this reason that by mixing 100 parts of common air with 100 parts of nitrous gas very variable absorptions were obtained. Secondly, the question of whether to introduce the nitrous gas into the tube before or after the air sample was also important, because if it was introduced first, both nitrous and nitric acids might be formed.

To avoid these two shortcomings Gay-Lussac conducted a nitrous gas test that employed an apparatus very similar to that used by Humboldt for assessing carbonic acid in a gas mixture or for analysing common air by means of nitrous gas and chlorine.[34] This test was performed in the following manner (Figure 5):[35]

The sample of the air to be analysed was collected in the measure (N), equivalent to 100 parts of the tube (K) graduated in 300 parts. The air sample was then introduced into this tube (K) with the copper funnel (M) coupled to the ferrule (HI) of the tube. The number of parts of the air sample contained in the tube was noted. Afterwards, the air sample was transferred to a wide glass vessel (A) with a flat bottom, containing about 250 parts and closed by a copper component (BFGC). This component consisted of a slightly funnelled part (BC), a funnel (FG) and a sleeve (DE) abraded with emery so that the ferrule (HI) of the tube (K) fitted exactly. The nitrous gas was measured in

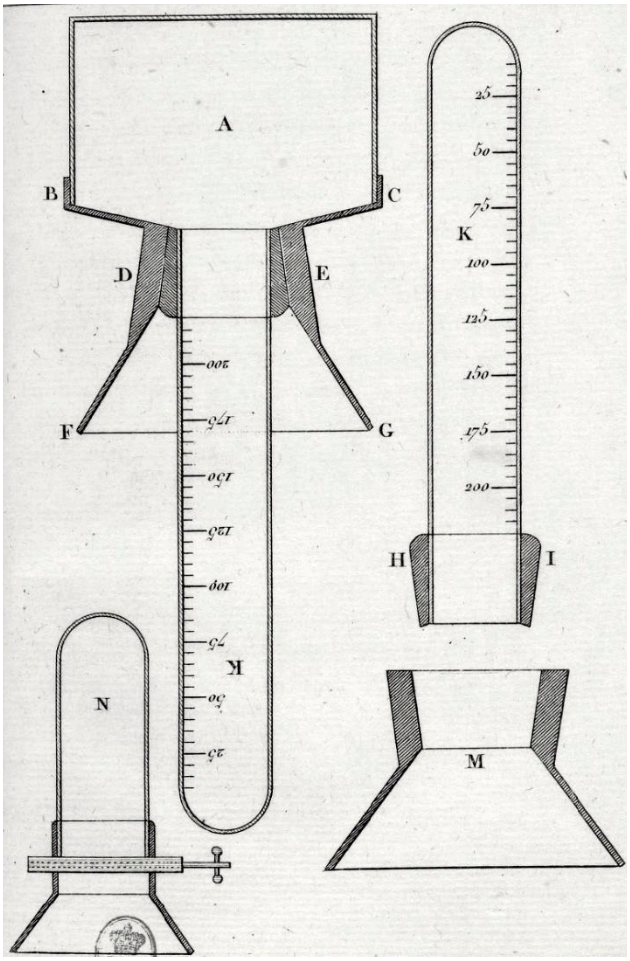

Figure 5. Gay-Lussac's nitrous gas eudiometer. From *Mémoires de physique et de chimie de la Société d'Arcueil,* 1809, Vol. 2, plate 2.

> *the same way and rapidly mixed with the air sample by coupling the tube to the sleeve (DE) without agitating. A red vapour appeared immediately and then disappeared very quickly. After half a minute, or one minute at most, absorption could be regarded as complete. The device was then turned upside down and the residual gas ascended in the tube. After that, the tube (K) was removed from the vessel (A) to restore the pressure equilibrium and the residue was assessed. The total absorption divided by 4 gave the quantity of oxygen.*

Gay-Lussac reported having performed many varied analyses, always finding a perfect agreement among them. In 1818, William Henry still regarded Gay-Lussac's application of nitrous gas to eudiometrical purposes as an accurate procedure, provided certain precautions suggested by his theoretical views of the constitution of nitrogen oxides were taken into account.[36]

FINAL REMARKS

The sources of Dalton's criticisms of the nitrous gas test were very precise: the influence of the size of the eudiometrical vessel and the shaking of the gas mixture in its volume reduction. He opted for the use of a narrow tube that allowed nitrous gas to be absorbed by water without shaking in an attempt to obtain nitric instead of nitrous acid. Nevertheless, he was aware that a greater reduction in volume was obtained if the test was performed over a broad surface of water. His assumptions about these two factors were in principle concerned with the justification of his statement on the multiple combining proportions, rather than with the improvement of the nitrous gas test, and he was in fact obliged to conduct the test in vessels of different sizes and with variable procedures until he obtained the results he was aiming for.

From 1806 onwards, Dalton contributed material as well procedural improvements to the nitrous gas test employed as a eudiometrical method. Thus, in addition to recommending the use of narrow tubes, he emphasised the advantage of adding the nitrous gas once the oxygen gas was already in the tube and not the other way around. Arguably, the nitrous gas test that in the hands of Dalton had evolved from a eudiometrical method to an iconic case of multiple combining proportions was returned to eudiometrists in a simpler and more trustworthy version of the eudiometrical test than those performed with the latest nitrous air eudiometers. In a certain sense, it was as if Priestley's conception of the nitrous air test, characterised by simplicity of materials, apparatus and experimental procedures, had won out in the end.

Dalton's investigations on the nitrous gas test engendered further developments in 1809 at the hands of Gay-Lussac, who had already begun his research work on eudiometry some years earlier. He did not agree with Dalton's experimental results on the proportions of combination of nitrous gas with oxygen, mainly because these proportions did not match his law of combining volumes. However, this discrepancy proved to be no obstacle to Gay-Lussac's acceptance of Dalton's conclusion on the influence of the size of eudiometrical recipients on the experimental outcomes. His own researches on the oxides of nitrogen, together with Dalton's recommendations on the size of the recipients, guided him in the reshaping of the nitrous gas eudiometer that culminated in a more definitive version of this type of instrument.

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The author wishes to acknowledge the Vernon Press for its permission to reproduce a number of excerpts from the author's book (see note 9).

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5. Upon contact of NO with atmospheric oxygen, a brownish gas [NO_2] forms immediately and the color dissipates within a few minutes as NO_2 dimerises to N_2O_4 and completely and irreversibly dissolves in water, giving a mixture of HNO_3 and HNO_2. Simultaneously, NO and NO_2 react to form N_2O_3, which also dissolves in water to give additional HNO_2. Consequently, a contraction in volume of the gas mixture is observed. In stoichiometric ideal conditions the global process would be: $6\ NO\ (g) + 2\ O_2\ (g) + 3\ H_2O\ (l) = 5\ HNO_2\ (aq) + HNO_3\ (aq)$. Therefore, the only residual gas with a common air sample in such conditions would be nitrogen. M. C. Usselman, D.G. Leaist, K. D. Watson, *ChemPhysChem*, **2008**, *9*, 106, p. 107.
6. J. Priestley, *Experiments and Observations Relating to various Branches of Natural Philosophy, with a Continuation of the Observations on Air*, J. Johnson, Birmingham, **1779**, p. 69. Chemists believed that phlogiston was an intangible fluid released in combustion that was impossible to handle. Atmospheric air was believed to consist basically of a mixture of phlogisticated or mephitic air (later called nitrogen) and dephlogisticated or vital air (later called oxygen). With regard to animal respiration, the prevailing belief was that expired air conveyed the phlogiston released from the lungs during breathing and evacuated it from the body. Phlogisticated air (i.e. saturated with phlogiston) was consequently unable to absorb more phlogiston and would not be appropriate for breathing; that is, it would be unhealthy or mephitic air. On the other hand, dephlogisticated air was deprived of more than its normal allocation of phlogiston, and therefore was more wholesome. In other words, the healthier an air the less phlogiston it contained.
7. J. Priestley, 1775, *Experiments and Observations of Different Kinds of Air*, J. Johnson, London, **1775**, pp. 20-21, 110-112.
8. This term is derived from two Greek words. The first part of the term (εὔδιος) means "clear or mild weather", but also with the implication of good air, because (διος) - stemming from Zeus - can mean "weather" or "air". The second part of the term (μέτρο) means "measure". M. Landriani, *Ricerche fisiche intorno alla salubrità dell'aria*, s.n., Milano, **1775**, pp. 3, 6.
9. To explore and comprehend how eudiometers work, the materials used in making them and the reagents employed in each eudiometrical test, all with special attention paid to the experimental procedures involved over the course of the test, constitute the main aims of the author's book. P. Grapí, *Inspiring Air. A history of air-related science*, Vernon Press, Wilmington, DE, **2019**. To understand eudiometers, it is essential to stress the interplay between the instruments themselves and their contextual environment and, in this sense, it is equally indispensable to emphasise that eudiometers took on a life of their own in many different contexts; human and animal health, quantification, gas analysis, chemical theory, medical therapeutics, plant and animal physiology, atmospheric composition, chemical compound composition, gas lighting, chemical revolution, experimental demonstration and the chemical industry.
10. Progress in the nitrous air test and eudiometer was mainly reflected in their use in research experiments and in the search to obtain a standard test procedure in order to arrive at a reliable test. The reliability of the test depended on many intrinsic and extrinsic factors, which were not always easy to define and control. However, the factors that proved to have the most significant effect were: the establishment of the test endpoint; the determination of the saturation ratio of nitrous and dephlogisticated air (oxygen); the dosing of the air samples; the time spent on particular operations; the water source used, and the

quality of the nitrous air as a reagent. Standardising the nitrous air test to make it more reliable involved working out an operating protocol that demanded skilful experimenters with the appropriate training. The issue was not that skilful experimenters such as Ingenhousz were able to execute that protocol successfully, but rather that novices in eudiometry would also be capable of performing it.

11. H. E. Roscoe, A. Harden, *A New View of the Origin of Dalton's Atomic Theory. A Contribution to Chemical History*, Macmillan and Co, London and New York, **1896**, p. 33.
12. A. J. Rocke, *Chemical Atomism in the Nineteenth Century. From Dalton to Cannizzaro*, Ohio University Press, Columbus, OH, **1984**, pp. 27-33.
13. A. J. Rocke, *Social Research*. **2005**, *72*, 1, 125, pp. 136-137.
14. W. C. H. Henry, *Memoirs of the Life and Scientific Researches of John Dalton*, The Cavendish Society, London, **1854**, p. 47. A. Thackray, *John Dalton. Critical Assessments of His Life and Science*, Harvard University Press, Cambridge, MA, **1972**, pp. 48-51, 64-66.
15. R. W. A. Oliver, M. Carrier, *The Library of John Dalton*, Titus Wilson & Son, Kendal, **2006**, pp. 9-14, 28-30.
16. J. Dalton, *Philos. Trans. R. Soc. London*. **1837**, *127*, 347, p. 348.
17. W. Henry, *An Epitome of Chemistry*, J. Johnson, London, **1803**, p. 74.
18. J. Dalton, *Memoirs of the Literary and Philosophical Society of Manchester.* **1805a**, 2nd series, *1*, 244, p. 249. A. F. Humboldt, *Ann. Chim*. **1798**, *28*, 123, pp. 151-171, 177-180.
19. Dalton gave no details of the size of this wide vessel.
20. A. J. Rocke, **1984**, 45, note 28. See note 12.
21. At that time, nitrous acid was not known to be a distinct and less oxygenated acid, but rather regarded as a mixture of nitric acid and nitrous gas. H. Davy, *Researches chemical and philosophical, chiefly concerning nitrous oxide*, J. Johnson, London, Biggs and Cottle, Bristol, **1880**, p. 31. *The Collected Works of Sir Humphry Davy*, (Ed.: John Davy), Smit, Elder and Co. Cornhill, London, **1836-1840**, 9 vols, Vol. 3, p. 22.
22. The first trial yielded the most oxygenated nitric acid [O + NO = NO_2, in Dalton's terms], while the second yielded the least oxygenated nitrous acid [O + 2 NO = N_2O_3, in Dalton's terms]. The latter reaction took place rapidly in the thin gas stratum of the wide vessel, but slow enough in the narrow tube to enable nitric acid to be the sole product (Usselman *et al*., 107. See note 5).
23. H. E. Roscoe, A. Harden, **1896**, p. 35. See note 11.
24. J. Dalton, **1805a**, pp. 247-251. See note 18.
25. The 136 [100 +36] parts of the mixture gave a residue of 79 parts in the first trial (assuming 21% of oxygen in common air). Therefore, the loss was 57 [136-79] and 7/19 [21/57] of the diminution was oxygen.
26. J. Dalton, *Memoirs of the Literary and Philosophical Society of Manchester*. **1805b**, 2nd series, *1*, 271, pp. 274-275, note. In this way, nitrous acid was formed, whereas when water was not present nitric acid was obtained, which required just half the quantity of nitrous gas. The replications of Dalton's experiments reported in his 1805 paper proved that in the narrow tube conditions (first trial) the greatest diminution in volume occurred at a ratio of 1.7, as Dalton reported. Nevertheless, the contraction in volume reported at a ratio of 3.4 (second trial) was significantly different from the replicated value. All in all, it is necessary to recognize that the influence of dissolved oxygen in water could make the second trial results plausible. The lack of published details on the exact size of the reaction recipients rendered a meaningful replication of the second trial impossible. (Usselman *et al*., **2008**, pp. 108-109. See note 5)
27. W. Henry, *An Epitome of Chemistry*, Collins and Perkins, New York, NY, **1808** (First American from the fourth English edition of 1806), pp. 153-154.
28. These tubes were of the same width but of shorter length than the one described by Dalton in 1805.
29. In 1904, the Council of the Manchester Literary and Philosophical Society resolved that photographs of the apparatus belonging to Dalton should be taken for reproduction in the papers of the Manchester Literary & Philosophical Society.
30. M. Crosland, *Gay-Lussac, Scientist and Bourgeois*, Cambridge University Press, Cambridge, **1978**, pp. 28-31.
31. J. L. Gay-Lussac, *Mémoires de Physique et de Chimie de la Société d'Arcueil*, Mad. V^e. Bernard, Paris, **1809a**, 3 vols, Vol. 2, pp. 206-234, 215-216, 218.
32. J. L. Gay-Lussac, 1809b, *Mémoires de Physique et de Chimie de la Société d'Arcueil*, Mad. V^e. Bernard, Paris, **1809b**, 3 vols, Vol. 2, 235, pp. 236-239. The study of the oxides of nitrogen was a complex field of research for early nineteenth century chemistry. Gay-Lussac successfully re-examined his conclusions on this issue in 1816, after Dalton's and Davy's criticisms (*Ann. Chim. Phys*. **1816**, *1*, 394).
33. Gay-Lussac's results on the composition of the oxides of nitrogen did not agree with those published by Dalton in 1805. According to Dalton, 21 parts of oxy-

gen could unite with 36 of nitrous gas or with twice 36, i.e. 72 parts. In other words, 100 parts of oxygen united with 171.4 or 342.8 parts of nitrous gas. In Gay-Lussac's opinion, these results were inaccurate because the first ratio of nitrous gas was too small and the second was too large, in addition to which the two gases did not combine in simple ratios. It should be remembered that Gay-Lussac's law of combining volumes established that gases combined in very simple ratios, and that the volume reduction they underwent on combination also had a simple ratio to their volume, or at least to the volume of one of them. (Gay-Lussac, **1809b**, p. 244. See note 32)

34. Ibid. pp. 246-247.
35. Ibid, pp. 249-251.
36. W. Henry, *The Elements of Experimental Chemistry*, Baldwin, Cradock and Joy and R. Hunter, London, **1818**, 2 vols; Vol. 1, pp. 393-394.