# John Dalton, the man and his legacy: the bicentenary of his Atomic Theory †

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The bicentenary of Dalton's paper, in which he set out his first "Table of the relative weights of the ultimate particles of gaseous and other bodies", provides us with the opportunity to reflect upon Dalton's life and achievements, to place his Atomic Theory in the context of its antecedents and to consider the views of some of his immediate successors.

# Introduction

On 21<sup>st</sup> October 1803 Dalton read a paper to the Manchester Literary and Philosophical Society on gas solubility, in which he set out a "Theory of the Absorption of Gases by Water." The last of the eight sections contains a sentence which Greenaway describes<sup>1</sup> "as among the greatest utterances of modern science." This reads "An enquiry into the relative

<sup>†</sup> The above illustration of John Dalton (reproduced courtesy of the Library and Information Centre, Royal Society of Chemistry) marks the 200th anniversary of his investigations which led to the determination of atomic weights for hydrogen, nitrogen, carbon, oxygen, phosphorus and sulfur.

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weights of the ultimate particles of gaseous and other bodies is a subject, as far as I know, entirely new; I have lately been prosecuting this enquiry with remarkable success." There follows a "Table of the relative weights of the ultimate particles of gaseous and other bodies."

The universal language of modern chemistry is that of chemical equations, and their alphabet is that of atoms. Such equations describe the conversion of reagents into products at the molecular level and thus express chemical change in quantitative terms. It was Dalton who first interpreted the facts of chemical combinations (*e.g.*, from Richter's equivalents) by a theory the essence of which, but not the details, have in Roscoe's words in 1895<sup>2</sup> "stood the test of time."

It is appropriate that this issue of *Dalton Transactions*, marking the bicentenary of the Daltonian Atomic Theory, should begin with an article reflecting on Dalton's life and scholarly contributions. The literature on this subject, much by professional historians of science, is vast. There is a comprehensive bibliography of works by and about Dalton up to 1997.<sup>3</sup> A selection of other important books, or parts of books, from the later part of the 20<sup>th</sup> century is to be found in references 3–7. The first biography was by W. C. Henry (the son

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of William Henry, of Henry's Law, a friend of Dalton);<sup>8</sup> he belatedly produced his fragmentary (according to Williamson Jones)<sup>9</sup> account in 1854, despite having been bequeathed Dalton's papers and named by Dalton as his official biographer.

Dalton was a prolific writer and correspondent. Many of his laboratory notebooks and manuscripts were in the archives of the Manchester Literary and Philosophical (M. L. & P.) Society. They were first researched by Roscoe and Harden, about 50 years after Dalton's death in 1844.<sup>2,10</sup> The 36, George Street home of the M. L. & P. was destroyed by fire in an air-raid of 24<sup>th</sup> December 1940, and with it much Dalton memorabilia; however, a metal box in the basement was saved, though the contents were badly damaged. Conservation work on the papers began in 1990. In April-June 1991 a selection of the conserved manuscripts was displayed in the John Rylands Library, Manchester, as part of an exhibition entitled "The Dalton Tradition" to mark the 150th anniversary of the foundation of the precursor to the Royal Society of Chemistry; an accompanying booklet by Leitch and Williamson provides a useful and succinct account of Dalton's life and achievements.11a

# John Dalton (1766–1844): a brief biography

Eaglesfield is a small village about 2 miles SW of Cockermouth and 12 miles NW of Keswick, Cumbria. Its place in history would be obscure were it not for having been the birthplace not only of Robert de Eglesfield (the founder of Queen's College, Oxford) but also, on about 5<sup>th</sup> September 1766, of John Dalton.

John was born in a simple thatched cottage. Its exterior has now lost its thatch, but above the doorway is an inscription, placed there towards the end of the 19<sup>th</sup> century, recording his birth, Fig. 1. Also to be found in Eaglesfield is one of the earliest Meeting Houses established in Cumberland by the Society of Friends (now a private dwelling); these would have been centres of both worship and much scholarly activity. [George Fox drew hundreds of Friends to hear him in the limestone outcrop at



Fig. 1 John Dalton's birthplace.

Pardshaw Crags in 1652 and again in 1663; the first Meeting House was built in Pardshaw (*ca.* 2 miles from Eaglesfield) in 1672.<sup>116</sup>]

The Daltons were Quakers. John's father, Joseph (1733–1787), married his wife, Deborah, at the Cockermouth Meeting House on June 10<sup>th</sup> 1755. There were six children though only three survived into maturity: Jonathan (1759–1834), Mary (1764–1788) and John. Joseph was a handloom weaver and plied his trade in the cottage. In 1786 he inherited 60 acres of land, which was entailed to Jonathan upon Joseph's death, and the land passed to John in 1834, having been willed to him by his brother; the entailment had been a matter of dispute between the brothers.<sup>12</sup>

Three men, all Quakers, were important influences on Dalton's early intellectual development: at Eaglesfield the schoolmaster, John Fletcher, and the amateur meteorologist, instrument maker and mathematician, Elihu Robinson; and later at Kendal, the blind polymath, John Gough, described by his pupil, the mathematician Whewell, as "a blind man, but very eminent in classics, mathematics, botany and chemistry" and Wordsworth agreed that Gough was the source of his remarkable description of a blind man in The Excursion.<sup>13</sup> Throughout his life Dalton acknowledged his debt to these teachers. In a letter<sup>14</sup> Dalton, at 22 years of age, wrote of Gough "He is a perfect master of the Latin, Greek and French tongues; the two former of which I knew nothing of six years ago . . . . . , but under his tuition have since acquired a good knowledge of them. He understands well all the different branches of mathematics . . . . . There is no branch of natural philosophy what he is well acquainted with .....; he can reason with astonishing perspicacity on the construction of the eye, the nature of light and colours .....; he is a good proficient in astronomy, chemistry, medicine, *etc.*"

Dalton was a pupil of John Fletcher at Pardshaw Hall School up to the age of eleven and by then, in his own words, he had "gone through a course of Mensuration, Surveying, Navigation, etc." 15 He received his introduction to mathematics from Elihu Robinson, and apparently was punctilious and persistent in obtaining solutions to knotty problems. At the age of twelve, perhaps in order to contribute to his family's income, he opened a school, initially in the family cottage and later at the Quaker Meeting House. The venture was not entirely successful, and so was abandoned and he worked on the land for the next two years or so. In 1781 he left for Kendal, then an important wool-trade town of about 5,000 inhabitants, to join his brother in teaching at the Quaker school of which their cousin, George Bewley, was principal. When the latter retired in 1785, the brothers took over; they offered to take in boarders and their sister, Mary, kept house. Fig. 2, from the copy in ref. 2,

JONATHAN and JOHN DALTON, Respectively inform their Friends, and the Public in general, that they intend to continue the SCHOOL lately tanght by GEORGE BEWLEY, Where Youth will be carefully inftructed in More Youth will be carefully inftructed in Anglish, Latin, Greek, and French; Auso Writing, Arithmetic Merchants Accompts, And the MATHEMATICS. The School to be opened on the 28th of March, 1785 N. B. Youth boarded in the Mafter's House on reafonable terms.

DALTON'S CARD.

Fig. 2 Dalton's card of 1785: the Kendal school.

shows Dalton's card of the time.<sup>16</sup> A circular, printed for the brothers in 1786, indicates that the range of subjects was increased to include *inter alia* navigation, geography, fluxions (calculus), conic sections, astronomy, optics, mechanics, pneumatics, hydrostatics and hydraulics.

According to a Mrs Cookson, a pupil in the school in 1785, but writing in later life,<sup>17</sup> "The school was not generally popular, owing to the uncouth manners of the young masters, who did not seem to have much intercourse with society; but John's natural disposition being gentler, he was more passable. I believe the last time of my going to Mr Dalton was about the year 1789. He was then becoming rather more communicative in his manner, but still a man of very few words."

Dalton's twelve years in Kendal were crucial to his intellectual development. He was a diligent observer and cataloguer of his environment. It was Gough who taught him to keep a meteorological diary; the first entry was 24th March 1787 and it was continued daily. The last entry, on the day of his death 27th July 1844, reads "a little rain this day." Dalton made his own thermometers and barometers, and supplied these to Peter Crosthwaite in Keswick. His readings in Kendal in the summer were taken at 6 a.m.; later, in Manchester, his thermometers were attached to a board outside his bedroom window and morning readings were taken at 8 a.m.18 His early Kendal data were compared with Crosthwaite's in Keswick in tabular form in his Meteorological Essays.<sup>19</sup> Dalton's rainfall measurements are a valuable historical record of fluctuations in rainfall in the NW region for a half century from 1787.<sup>18</sup> In Kendal, Dalton collected plants, pressed them, and offered them to Crosthwaite for his Keswick museum, noting:<sup>20</sup> "I have at length completed the book of plants and made an index both to the Linnaen and English names." He made observations on the metamorphosis of caterpillars. In 1787, he gave a course of twelve public lectures in Kendal on mechanics, optics, pneumatics, astronomy, and the use of globes, to which he added a lecture on fire; the charge for the original course was 10s., the latter 5s., and evidently they were financially unprofitable. Dalton contributed to the then popular cultural magazines, Gentlemen's Diary and Ladies' Diary, by submitting solutions to mathematical, scientific and ethical questions, and gained prizes. In 1790 he measured his own intake of food and loss by excretion in order to determine the loss by respiration and perspiration. Perhaps this was a prelude to his aspiration to change the course of his career in favour of medicine (or law). Thus, in 1790, he wrote to Elihu Robinson, his uncle Thomas Greenup, and George Bewley, seeking their advice as to his "inclination to quit my present Profession of a Teacher and enter upon some others where they may be an Expectation of Greater Emoluments."<sup>21</sup> He received little encouragement but sensed that the "Practice of Physic"<sup>21</sup> might be his best course. He cited his interests in "Botany and Chymistry;"<sup>21</sup> he claimed some familiarity with Boerhaave's Treatise, Watson's Essays, and Boyle's Chemical Tracts, the style of which he declared to be "tedious and verbose."<sup>21</sup> In his Kendal years, except for Gough and Crosthwaite, Dalton was scientifically isolated and had access to very little original literature.22

Dalton left Kendal for Manchester, to which he was no stranger, upon his appointment (with Gough's recommendation), early in 1793, as tutor of mathematics and natural philosophy in the New College. This institution, founded in 1786, was a Dissenting Academy (a successor of the Warrington Academy, of which Joseph Priestley had been its most illustrious teacher), non-conformists having been barred from entry into Oxford and Cambridge. Among its governors were the officers of the Manchester Literary and Philosophical Society (M. L. & P.). The latter had been founded in 1781 and was headed by three distinguished scholars: Thomas Percival, Thomas Barnes and Thomas Henry. Henry had translated Lavoisier's *Opuscules* in 1776, and thus was instrumental in promoting an interest in the advances in chemistry made in France; "Henry's Magnesia" became a lucrative proprietary medicine. His son, William, (eight years Dalton's junior, but a firm friend) followed the father (Thomas) and preceded the son (W. C.) as F.R.S. and was a Copley Medallist. He gave a course of public lectures on chemistry in 1798-1799, for which a forty page syllabus was sold for 1s. Dalton had earlier (1796) attended a course of twelve lectures, also in Manchester, by Thomas Garnett (who in 1799-1800 was President of the Royal Institution). Dalton joined the M. L. & P. in 1794, having been proposed by Robert Owen, attended his first meeting on the 3rd of October, and read his first paper on the 31st of October ("Extraordinary facts relating to the vision of colours, with observations;" ref. 3, p. 36). He became Secretary in 1800, Vice-President in 1808, and was President from 1817 until his death. He read 116 papers to the Society, according to Partington,<sup>7</sup> "many of little importance"; this is surely a just comment only on the work of his later years.

When Dalton arrived in Manchester, the city had already begun its metamorphosis from a rural to an industrial environment. The first official census showed that in 1801 there were about 70,000 inhabitants; by the time of Dalton's death there had been a population explosion, as Manchester had become a major centre of the Industrial Revolution. Cotton-spinning, dyeing and calico printing were of prime importance and the city had one of the first public gas works. Several of Dalton's M. L. & P. associates showed an interest in the application of chemistry to industry, although only one or two of Dalton's papers have an industrial slant (see for example ref. 23).

Dalton resigned from the New College (which moved to York) in 1800 and thereafter supported himself by private teaching, occasional lecturing and undertaking commercial analyses (*e.g.*, for the bleachers, Sykes of Edgely). He worked from a room in the M. L. & P.'s house in George Street. During 1824–1825 he gave a course of lectures in pharmaceutical chemistry at the then newly inaugurated Pine Street Medical School.

Initially, Dalton lodged at the college, later joined a fellow Quaker at nearby 35, Faulkner Street, then lived (1804–1832) with the family of the Rev. William Johns at 10, George Street; in his last years he was looked after by a housekeeper at 27, Faulkner Street.

Dalton spent his mornings in teaching, his afternoons in experimental work, sometimes with pupils in attendance, and his evenings alone in the laboratory. Whilst his was not a compelling personality as a lecturer, he seems to have had an easy relationship with young people, as evident from an account of Dr Charles Clay. The latter related how in his youth Dalton had sent him on an errand to collect some marsh gas (methane) in bottles from a mine, and then challenged him to find a solution to the problem of transferring the contents, without mixing with the atmosphere, into a pneumatic trough.<sup>24</sup> Farrar has pointed out that Dalton seems to have liked teaching,<sup>25</sup> and Cardwell noted that "he thought in simple, concrete terms as one might suppose would suit a teacher; and this would be consistent with his simple and realistic view of the atomic theory. He liked playing with models, both as aids to teaching and as representations of physical reality."26 (Such threedimensional models of balls and sticks, made for Dalton by his friend, the civil engineer and cotton manufacturer, Peter Ewart in 1810, are exhibited in the Science Museum, London.) Dalton's most famous pupil, James Joule, studied with him from the age of fourteen in 1832 until 1837 (the time of Dalton's first stroke); others included the engineer-mathematician Eaton Hodgkinson (who came in his twenties) and the pioneer gas engineer Samuel Clegg.

Dalton had early gained a reputation outside Manchester through his work on gases. Thus, in 1803,<sup>27</sup> and again in 1809, he was invited to lecture at the Royal Institution; he had previously only been in London to buy instruments. His meeting with Thomas Thomson (who had been William Henry's

teacher) in 1804 at Henry's house was important, since Thomson in his influential book of 1807 was the first to give publicity to Dalton's Atomic Theory,<sup>28</sup> and was instrumental in Dalton's invitation to lecture in Edinburgh and Glasgow in the same year. It was on his return that Dalton began to write his *New System*,<sup>29</sup> which contained many of the ideas which were first printed in the lecture course of 1805.<sup>27</sup> In 1822, he went to Paris and met many of its most eminent scientists, several at their places of work (unlike his experience with their counterparts in London), including Ampére, Berthollet, Biot, Cuvier, Gay-Lussac and Thénard. In 1835, Dalton attended the British Association Meeting in Dublin; he was to have been President at the B. A.'s Manchester Meeting of 1842, but was then too ill to officiate and was given the title of Vice-President.

According to Partington (p.760 of ref. 7), "Dalton was somewhat above middle height, with a robust and muscular frame, capable even in his later years of great physical exertion." This is evident from Ross' recently published record of Dalton's Lakeland Excursions, Helvellyn having been ascended by him at least 40 times.<sup>30</sup> The first record of such excursions is in Dalton's letter to Peter Crosthwaite of 23rd August 1794, which includes the following passage: "I was up at Buttermere & had 3 companions, but we did not proceed to Borrowdale; we were upon the Red Pike and viewing Scale Force, but I had not then my Barometer. Upon the Red Pike we see at one Station 5 of the Lakes, viz. Ennerdale, Loweswater, Crummock, Buttermere and Derwent. Grasmere is a very rough Hill to climb, the worst I was ever upon;- The ascent to the Red Pike by way of Scale Force is tolerable, but our Descent by Sour Mill Beck was most hideous." Jonathan Otley gave a summary of his Lakeland expeditions with Dalton, beginning in 1812 and ending with their last trek in Dalton's seventieth year in 1836: <sup>31</sup> "A climb of Helvellyn. Dalton was still taking his observations of dew points, and had brought a large bottle to obtain a sample of air from the summit for subsequent analysis." In his introduction to a paper published in 1824,32 Dalton noted "I had for some years, been in the habit of allowing myself a week or two in the summer for relaxation from professional engagements, and had generally spent the time in breathing the salubrious air of the mountains and lakes near my native place, in the North of England." He liked his pipe and a glass of ale and in Manchester enjoyed his weekly game of bowls. There are ample records of several acts of kindness and happy relationships with friends. He remained a bachelor, but in his letters he often wrote with affection and admiration of women. This is illustrated by the following four brief excerpts,<sup>33</sup> taken from a letter of 1809 to William Johns, cited in ref. 9, about his journey to the R. I. in 1809, and his reception there (Wollaston and Davy were then joint secretaries of the Royal Society): (i) " & paid my fare to Northampton. We got an addition of 2 Gentlemen & another young Lady for London: it was a fine night & soon we found ourselves very comfortable and warm. I had two top coats, one on & the other on my knee: which last was very serviceable both to myself & the two Ladies (who were but thinly clad) one of whom sat opposite & and the other on my left. I tucked it round us frequently, but it was soon off & I had to do it again; however we crept very close together." (ii) "I had not finished my sleep with the two young Ladies & it seemed a pity to let go a pleasure which one cannot always command." (iii) "I should tell Mrs J. something about the Fashions here; but it is so much out of my province that I feel rather awkward. I see the Belles of New Bond Street every day, but am more taken up with their faces than their dresses. I think blue & red are the favourite colours. Some of the Ladies seem to have their dresses as tight round them as a drum. Others throw them around them like a blanket. I do not know how it happens, but I fancy that pretty women look well either way." (iv) "On Tuesday I had my 3<sup>rd</sup> Lecture: after which I went to dine at a Tavern to meet the chemical club. There were 5 of us; two of whom were Wollaston & Davy, Secretaries of the Royal Society: we had much discussion on chemicals. Wollaston is one of the cleverest men I have yet seen here." Dalton was unaffected, speaking with a marked regional accent. Cardwell notes<sup>26</sup> that he was a life-long devout and conscientious member of the Society of Friends, although in his writings there are no records of expressions of religious (or political) opinions.

The French elected Dalton a corresponding member of the Academie des Sciences in 1816 and raised him to one of only eight Foreign Associates in 1830. His F.R.S. came in 1822 (in 1810 he declined to be nominated), and in 1826 he became the first recipient of the Royal Medal, presented to him by Davy, then President of the Royal Society, "for the development of the chemical theory of Definite Proportions, usually called the Atomic Theory and for various other labours and discoveries in physical and chemical science." Dalton was also honoured by the academies of Berlin, Moscow and Munich. Oxford awarded him the D.C.L. in 1832 (in company with Faraday), and Edinburgh the Ll.D. at its B.A. Meeting in 1834. At the instigation of Babbage, Dalton gained a Civil List Pension of £150 p.a. in 1833 (raised to £300 p.a. in 1836), and was presented to William IVth at Court in 1834. In the same year Francis Chantrey accepted the commission (for £2000, raised by a Manchester committee) to sculpt a statue of Dalton, delivered in 1838 and now in the Manchester Town Hall.

Smyth noted<sup>3</sup> that the three main sources of portraits were the W. Allen painting of 1814, a replica of which (Fig. 3) is now at the M. L. & P. (the original was destroyed in the air-raid of 1940, together with Ford Maddox Brown's 1886 famous painting of "Dalton collecting marsh fire gas"), the 1834 drawings made by Chantrey (now in the National Portrait Gallery, London; it also has T. Phillips' portrait of 1836), and the J. Nicklin daguerrotypes of 1842. One of the latter is at the M. L. & P., and another at the Science Museum, which also has copies of a left and a right profile of C. F. Carter's medals struck in 1842 in honour of Dalton and in commemoration of the B. A. Meeting of that year.



Fig. 3 John Dalton: the M. L. & P. replica of the W. Allen portrait of 1814.

Dalton suffered the first of several strokes in April 1837. His last paper <sup>34</sup> to the M. L. & P. was read three months before his death on 27<sup>th</sup> July 1844. He was accorded a public funeral: his coffin at the Old Town Hall was visited by some 40,000 people, and the funeral procession on the way to his burial at the Ardwick Cemetery was said to be about a mile in length.<sup>35</sup> Dalton left £800 and six houses. His original intention had been to endow a Chair of Chemistry at Oxford, but in a codicil to his will he named the family of Rev. Johns (which had fallen on hard times) as his legatees. The bulk of his estate was later passed on to the grand-daughter of his cousin, George Bewley, who ultimately left several items of Dalton memorabilia to Manchester University's Dalton Hall.

# Dalton's apparatus and some comments on his prowess as an experimentalist

Farrar's 1966 article<sup>25</sup> on Dalton's Scientific Apparatus makes it abundantly clear that Roscoe's rather romantic view<sup>36</sup> of the simplicity of Dalton's equipment requires revision. A collection was catalogued and preserved at the M. L. & P., but regrettably almost all was destroyed in the air-raid of 1940. However, photographs taken in 1904,37 some of which are reproduced in ref. 25, include thermometers, barometers, manometers, glass lenses, specific gravity bottles and bulbs, a pair of scales with a set of brass weights, a balance made by Accum with a box of weights in brass and the smallest in platinum, a glass tube used by Dalton for measuring the tension of carbon disulfide vapour, a hydrometer, eudiometers and cubical flasks. Dalton possessed "a valuable selection of apparatus" 38 from John Sharpe, had access to the equipment of William Henry and had purchased for £200 apparatus from the then leading scientific supplier, W. and S. Johns.

The freezing point graduated mercury thermometer, stamped J. D. 1823, was tested in 1904 by Baxendell, who noted <sup>39</sup> that the freezing point was about 1/3 °F below the mark on the stem. Benjamin Silliman heard Dalton give a popular lecture at the M. L. & P. to a large audience "attended by attractive young ladies and laymen of varied interests ..... Dr Dalton exhibited one experiment which I never saw so well performed before," and commented on the simplicity of the glass apparatus Dalton had used to "establish his famous gas law."<sup>40</sup>

Examining Dalton's Table of Atomic Weights (Fig. 4<sup>41</sup>), the reader may readily form the impression that Dalton was a poor experimentalist, neglecting the more significant point that the discrepancies with current data are in large measure due to Dalton's erroneous postulates (e.g., that water is HO and ammonia is HN; here and elsewhere, unless otherwise stated, we shall use modern names and/or formulae; for Dalton's symbols and his representation of some compounds, see Fig. 5<sup>42</sup>). In a 1969 article on " Dalton as Experimenter",<sup>43</sup> Trengove showed that the view, which had gained some currency in the 19th century,44 that Dalton was a poor experimentalist required revision. Among Dalton's data cited<sup>43</sup> were the following items. (i) Repeated experiments on the reaction of NO with O<sub>2</sub> to give NO<sub>2</sub>, led Dalton to the correct conclusion of 2 vols. NO + 1 vol. O<sub>2</sub>. (ii) Using his rather obscure "nitrous gas method for determining atomic weights of some metals" (*i.e.*, measuring the volume of NO obtained by dissolution of a metal in nitric acid or, for gold,<sup>45</sup> aqua regia), Dalton obtained respectable values (Table 1<sup>43</sup>). (iii) Table 2<sup>43</sup> shows Dalton's results<sup>46</sup> of his efforts to obtain "atomic weights of fixed alkalis and the earths" from analyses of K<sub>2</sub>CO<sub>3</sub>, K<sub>2</sub>SO<sub>4</sub>, KNO<sub>3</sub> and KCl.

Partington notes that:<sup>47</sup> (a) in 1805 Dalton described his results on the combustion of CH<sub>4</sub>, C<sub>2</sub>H<sub>4</sub> ("olefiant gas") and CO which were consistent with the equations CH<sub>4</sub> + O<sub>2</sub> = CO + H<sub>2</sub> + H<sub>2</sub>O (condensed), C<sub>2</sub>H<sub>4</sub> + O<sub>2</sub> = 2CO + 2H<sub>2</sub> and 2CO + 2H<sub>2</sub> + 2O<sub>2</sub> = 2CO<sub>2</sub> + 2H<sub>2</sub>O (condensed); (b) in 1819 Dalton Table 1 Comparison of Dalton's and modern values on the composition of four  $\mathsf{oxides}^{43}$ 

		Parts of oxygen to 100 parts of metal		
Met	al	Dalton	Modern	
Nicl	kel	27.0	27.3	
Cop	per	12.5	12.6	
Silv	er	7.7	7.4	
Mer	cury	4.0	4.0	

Table 2 Comparison of analyses of some potassium salts from acid / KOH reactions  $^{43}$ 

	Acid / base (%)	
Compound	Dalton	Modern
Carbonate of potash, K <sub>2</sub> CO <sub>3</sub> Sulfate of potash, K <sub>2</sub> SO <sub>4</sub> Nitrate of potash, KNO <sub>3</sub> Muriate of potash, KCl	31.1 / 68.1 44.7 / 55.3 47.5 / 52.5 34.4 / 65.6	31.9 / 68.1 46.0 / 54.0 51.9 / 48.1 36.9 / 63.1



Fig. 4 Dalton's Table of Atomic Weights.<sup>41</sup>

found that 10 vols. of  $(C_2H_5)_2O$  vapour on explosion in a eudiometer required 60 vols. of  $O_2$  and gave 40 vols. of  $CO_2$ ; (c) determined the vapour density of  $(C_2H_5)_2O$  by "evaporation in a vacuous globe and measuring the pressure on a mercury manometer;" and (d) by experiments similar to (a)–(c), noted that the gas formed on cracking whale oil was "a mixture of olefiant gas, and a new one of double its power . . . . . . super olefiant gas."<sup>23</sup> The former we now know as  $C_2H_4$  and the latter (discovered by Dalton) as  $C_4H_8$ .

Some quantitative (but non-chemical) reasonably accurate Daltonian observations are noteworthy, and include (i)–(iii). (i) The height of the Auroral Arch was estimated to be 150 miles, by simultaneous observations, using a Dolland theodolite, by

#### NEW TABLE

#### OF THE RELATIVE WEIGHTS OF ATOMS.

At the close of the last volume, the weights of several principal chemical elements or atoms were given; but as several additions and alterations have been educed from subsequent experience, it has been judged expedient to present a reformed table of weights.

#### SIMPLE ELEMENTS.

Weights.	Weights.
Hydrogen	Strontium
Azota $5+ \text{ or } 10^{2}$	Antimony40
Carbone 5.4	Iridium
Oxygon 7	Palladium
Dhomhomia 9	Uranium
Sublan 13 or 14	Tin
Calainer 17?	Copper
Calcium	Rhodium 56
Sodium	Titonium 50 ?
Arsenic	Cold 601
Molybdenum21, or 42?	Parium 61
Cerium	Darium
Iron20	Bismuth
Manganese25	Platina
Nickel	Tungsten
Zinc	Silver90
Tellurium29, or 58?	Lead90
Chromium	Columbium107 ? 121 ?
Potassium35	Mercury167, or 84?
Cobalt	
SIMPLE OR	COMPOUND ?
Weights.	Weights.
Fluoric Acid 10? 15?	Muriatic Acid 2 20 or 21
Magnesia	Gas 500, 01 51
Alumine	Zircone
Chuging	Silex 45?
Time 94	Yttria
Omenaniotic Apid	
(Llaring) 20 or 30	
(chlorine) 29 01 30	

Fig. 5 Dalton's symbols and his representation of some compounds.<sup>42</sup>

Dalton in Kendal and Crosthwaite in Keswick on 15<sup>th</sup> February 1793; previous estimates ranged from 1000 feet to 1000 miles.<sup>48</sup> (ii) Dalton's measurement of the maximum density of water in 1799 led him to the value 42.5 °F (the correct value is 39.3 °F).<sup>49</sup> (iii) Dalton derived the height of Helvellyn as 3105' from barometric pressure readings (the Ordinance Survey gives 3118').<sup>50</sup>

#### **Dalton's scholarly contributions**

Dalton's lasting fame rests on his *Atomic Theory*, closely linked to his *Law of Multiple Proportions*. These, as well as his *Law of Partial Pressures*, are discussed in the next section and are placed in the context of earlier and selected subsequent discoveries by others. In the two concluding paragraphs of the preceding section, some significant contributions of Dalton were also outlined.

Dalton's first published work is his meteorological book of 1793,<sup>19,51</sup> which did little to advance the subject in an original fashion.<sup>52</sup> The earlier parts dealt with instruments (thermometers, barometers, hygrometers), then heat (caloric), clouds, thunderstorms, and a local high wind in Windermere. The last part, concerned with the *Aurora Borealis* (see also previous section), shows significant originality. Dalton concluded that its light was not caused by combustion but by "electric light" and that it was a magnetic phenomenon because of its symmetry about the magnetic meridian; in the preface to the book Dalton conceded that Halley had come to the same conclusion regarding magnetism.<sup>53</sup> In March 1799, Dalton read a paper to the

M. L. & P.<sup>54</sup> which contained the first definition of *dew-point*<sup>55</sup> and the conclusion that springs are fed by rain. He measured the temperature of cold spring water which caused the deposition of dew on the outside of a glass cup; this is the basis of the Daniell hygrometer. In the same year, he showed that *water is a heat conductor*,<sup>49</sup> contrary to Rumford's theory.

Although Lavoisier had established that the principal constituents of the atmosphere are nitrogen and oxygen, there were three prevailing views at the turn of the 18/19<sup>th</sup> century: that air was (i) a compound of the two (the contemporary proponent was Thompson<sup>28</sup>), (ii) in a state of solution, similar to that of salt in water (advocated by Berthollet), and (iii) "an intimate mixture." Dalton had to press his correct assertion (iii), the *Theory of Mixed Gases*,<sup>56</sup> "in the face of very formidable opposition from most of the leading scientists and from textbook writers of the time and, only W. Henry was, at first, in favour of Dalton's views."<sup>57</sup> Dalton independently (see also Gay-Lussac) made observations on the expansion effect of heat on gases (air, H<sub>2</sub>, O<sub>2</sub>, N<sub>2</sub>, CO) and concluded that "all fluids under the same pressure expand equally by heat;"58 this is essentially *Charles' Law.*<sup>59</sup> [In the first decade of the 19<sup>th</sup> century, Dalton was much preoccupied with heat and related matters, but unfortunately he had a lifelong firm adherence to the erroneous caloric theory;<sup>60</sup> he believed in the physical reality of caloric, the weightless and highly elastic fluid which he supposed surrounded the atoms of all bodies, especially gases.]

The first communication which Dalton made to the M. L. & P., read on October 31st 1794, was concerned with the phenomenon now generally, but erroneously, called "colour blindness",<sup>61</sup> a condition which in many languages (including French, Russian and Spanish) is still called "Daltonism".6 Dalton became aware of the peculiarity of his vision from observations on a pink geranium, and noted that his brother's vision was the same as his,<sup>63</sup> and that brothers in a few other families were similarly affected; hence their unusual vision was hereditary. An extract from ref. 61,63 reads "The flower was pink, but it appeared to me almost an exact sky-blue by day; in candle-light, however, it was astonishingly changed, not having then any blue in it, but being what I called red, a colour which forms a striking contrast to blue. Not then doubting that the change of colour would be equal to all, I requested some of my friends to observe the phenomenon, when I was surprised to find that they all agreed, that the colour was not materially different from what it was by day-light, except my brother, who saw it in the same light as myself." Dalton was convinced that the condition was due to a blue coloration in the vitreous humour of the eye, and instructed that a postmortem examination on his eyes should eventually be carried out. On the day following his death, this took place and revealed that the humours of one eye were "perfectly pellucid"; the eyes were not discarded but stored, in air, and are now in the Museum of Science and Industry, Manchester. The correct explanation of Daltonism was proposed (but not accepted by Dalton) by Young in 1802,<sup>64</sup> now known as the three-component receptor theory; a DNA analysis extracted from the preserved eye in 1995 showed that Dalton was a deuteranope, lacking the middlewave photopigment of the retina.<sup>62</sup>

A curiosity of Dalton's work is his book on *Grammar*.<sup>65a</sup> While it is unlikely that it had much influence, it had some favourable reviews.<sup>65b</sup> It was founded on philosophical principles: "Grammatically speaking, there are three times, present, past and future; although strictly and mathematically speaking, we can admit only two, past and future." Greenaway points out that this passage "gives some idea of Dalton's method."<sup>65b</sup>

# **Atomic Theory**

John Dalton is justifiably known as the father of modern atomic theory, but by a mixture of bad luck and stubbornness he failed to make as much of his ideas as was possible. His contemporaries, particularly Gay-Lussac, Berzelius, and Avogadro, recognised the importance of his work and took it forward to something close to our modern view.

The concept of atoms was put forward by the Greeks Leucippus and Democritus about 440 B. C., and although this was later opposed by Aristotle and all who followed his scientific philosophy, the concept had steady support right through to Dalton's times. In 1588 Giordano Bruno wrote "The division of natural things has a limit; an indivisible something exists." Pierre Gassendi (1592–1655) was a strong supporter, and he described the Greek position as follows: atoms cannot be created or destroyed, they are solid, have weight, and cannot be divided; they have a definite size although this is very small. In later years both Robert Boyle (he used the word corpuscles) and Isaac Newton (his primitive particles) were atomists.<sup>66-68</sup>

The idea that atoms could be held together to form more complicated groups was also favoured by some early workers, notably Gassendi.<sup>69</sup> However, a conclusive proof of the law of Constant Composition, came from the experiments of Proust who showed that the composition of copper carbonate, when synthesised by dissolving copper in acid and then forming the precipitate by adding sodium carbonate, was the same as the naturally occurring copper carbonate 'malachite green' ("... is it not right to believe that the native carbonate of copper will never differ from that which art produces in its imitation?").<sup>70,71</sup> Although this law had its early opponents, most notably Berthollet, it was soon accepted as a tenet of chemistry, not least because many people had believed it to be true even before Proust's work.

The birth of modern chemistry is usually taken as the publication of Lavoisier's book "Traite Elementaire de Chimie" in 1789. In 1777 he had put forward a new theory of combustion by postulating the role of oxygen (Priestley's dephlogisticated air which Lavoisier called pure air),<sup>72</sup> and later (1783) he launched his attack on phlogiston theory.<sup>73</sup> Lavoisier's work was distinguished by its emphasis on quantitative measurements, and his book contained a clear statement of the conservation of mass in chemical change. A book was published in 1787, jointly by de Morveau, Lavoisier, Berthollet, and de Fourcroy, called "Methode de Nomenclature Chimique," in which systematic names for chemical compounds were substituted for trivial names. The book also contained proposals for new chemical symbols by Hassenfratz and Adet; an English translation appeared in 1788.

So, when Dalton started on his atomic theory chemistry had moved well beyond its alchemical roots and was firmly founded on quantitative studies. Most of the laws of stoichiometry (a term introduced by Richter to describe the quantitative laws of chemical composition) had been formulated, and Richter's law of equivalents enabled the first table of equivalent weights to be produced in 1792.<sup>74</sup> Richter had established that in chemical reactions (mainly acids with bases), definite proportions by weight were found for the reactants, and this was a key step towards Dalton's deduction of atomic weights.

Dalton's first scientific experiments stemmed from his lifelong interest in meteorology, referred to earlier. One of his most important scientific conclusions was that water is a component of air at all temperatures, and he produced a table of the vapour pressure of water at different temperatures from his own experiments.<sup>75,76</sup> This work led on to what is now called the Law of Partial Pressures. The most important source of his work on the pressures of mixed gases is four essays read to the M. L. & P. in 1801. In the first volume of his famous book he says "When any two or more mixed gases acquire an equilibrium, the elastic energy of each against the surface of the vessel, or of any liquid, is precisely the same as if it were the only gas present occupying the whole space and all the rest were withdrawn."<sup>77</sup> Whilst the law is true for perfect gases, the premise on which it was proposed is false; Dalton says: "The distinguishing feature of the new theory, was that the particles of one gas are not elastic or repulsive in regard to the particles of another gas, but only to the particles of their own kind."<sup>78</sup> A better view, which could have been given at the time, would be that in a gas all particles are equally elastic or repulsive one with another; the truth lies in the kinetic theory of gases produced later.

Dalton's first table of atomic weights (for 6 elements and the weights for 15 molecules based on their assumed composition) was presented as a supplement to a paper on the absorption of gases by water, which was read to the M. L. & P. in 1803, and published in 1805.78 There has been much speculation on the way in which this table derived from Dalton's work on gases, notably by Roscoe and Harden,<sup>10</sup> by Nash,<sup>79</sup> and by Partington.<sup>7</sup> Nash believed that the atomic weights were introduced to provide some explanation of the fact that different gases had different solubilities in water. Dalton wrote as follows:<sup>78</sup> "Why does water not admit its bulk of every gas alike? This question I have duly considered, and although I am not yet able to satisfy myself completely, I am nearly persuaded that the circumstance depends on the weight and number of the ultimate particles of the several gases." However, in a footnote he says that subsequent experience renders this conjecture less likely. He goes on to say (as noted in our introduction): "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." In lectures to the Royal Institution in 1810 Dalton himself attributed the origins of his atomic theory to his studies on the properties of mixed gases.

The first important new idea in Dalton's Atomic Theory was that atoms of different elements had different masses, and he arrived at this conclusion by deciding that they were not of the same size. He said: 80 "That every species of pure elastic fluid (gas) has its particles globular and all of the same size; but that no two species agree in the size of their particles, the temperature and pressure being the same." He preceded this with an important statement: "At the time (1801) I formed the theory of mixed gases, I had a confused idea, as many have, I suppose, at this time, that the particles of elastic fluids are all of the same size; that a given volume of oxygenous gas contains just as many particles as the same volume of hydrogenous gas." In deciding that different particles did not have the same size he was led to discard the important principle that equal volumes of a gas at the same temperature and pressure have the same number of molecules, which was later to be deduced by Avogadro from Gay-Lussac's observation that gases undergoing chemical reactions did so in simple volume proportions (one to one, one to two, etc.).

Dalton's most important step leading to atomic weights lies in his recognition of the law that we now call the Law of Multiple Proportions: "If two elements combine to form more than one compound then the relative weights of the second element which combines with a fixed weight of the first element will be small round numbers." Thus in carbon monoxide and carbon dioxide the ratio of the weight of oxygen is 1 : 2. There are many exceptions of course; in SO<sub>2</sub> and SO<sub>3</sub>, the oxygen ratios are 1 : 1.5 with respect to a fixed weight of sulfur, or 1 : 2/3with respect to a fixed weight of oxygen. However, the rule had wide validity for compounds known at the time, and the simplest deduction from it was that compounds had simple formulae and atoms definite weights.

In calculating his atomic weights Dalton adopted general rules about molecular composition based on the compounds known at the time. His first, and most important, rule was:<sup>81</sup> "When only one combination of two bodies can be obtained, it must be presumed to be a binary one, unless some cause appear to the contrary." It is an excellent rule given the inclusion of the word 'cause' and was adopted by many others. But of course the rule is generally invalid because atoms have

different valencies, a concept that was not introduced until the middle of the  $19^{th}$  century. Dalton's other rules such as "when two combinations are observed they must be presumed to be a binary and a ternary", and that when three are observed we may expect one binary and two ternary, *etc.*, are invalid, for the same reason.

Dalton goes on to say: "from the application of these rules, to the chemical facts already well ascertained, we deduce the following conclusions:  $1^{st}$ . That water is a binary compound of hydrogen and oxygen, and the relative weights of the two elementary atoms are as 1 : 7, nearly;  $2^{nd}$ . That ammonia is a binary compound of hydrogen and azote (*nitrogen*), and the relative weights of the two atoms is 1 : 5, nearly." The atomic weights he derived from these rules were almost all based on the quantitative measurements of others.

The correct formulae of water and ammonia were deduced in 1811 by Avogadro, who saw the implications of Gay-Lussac's law of combining volumes. In 1809 Gay-Lussac gave 16 examples of gas reactions in which the volumes of the interacting gases were in simple proportions; one of these was that 100 volumes of oxygen combined with 199.89 volumes of hydrogen (the deviation from 200 was attributed to a small amount of nitrogen in the hydrogen), and another (due to Berthollet) was that 100 volumes of nitrogen combined with 300 volumes of hydrogen to give 200 volumes of ammonia.<sup>82,83</sup> Dalton himself repeated experiments on the decomposition of ammonia, by passing the gas through a red hot tube, and found that on average 26 volumes of nitrogen were produced for 74 volumes of hydrogen.<sup>84</sup>

Gay-Lussac said that his observations were very favourable to Dalton's ingenious idea about the composition of molecules, "that combinations are formed from atom to atom, the various compounds which two substances can form would be produced by the union of one molecule of the one with one molecule of the other, or with two ....."<sup>82</sup> Avogadro also recognised the importance of Dalton's work, saying "... our hypothesis, which is at bottom merely Dalton's system furnished with a new means of precision from the connection we have found between it and the general fact established by M. Gay-Lussac."<sup>85</sup> Avogadro calculated from the gas densities measured at the time that the atomic weight of nitrogen was 13.238 and that of oxygen 15.074, both relative to that of hydrogen as 1. Avogadro was also the first to establish that molecules like hydrogen were diatomic, a possibility not recognised by Dalton.

Dalton seems never to have accepted the implications of Gay-Lussac's and Avogadro's work. In a letter to Berzelius, in 1812 he said: "The French doctrine of equal measures of gases combining is what I do not admit, understanding it only in a mathematical sense. At the same time I acknowledge there is something wonderful in the frequency of the approximation." Even in 1827 he said, "Combinations of gases in simple ratios occur but they are only approximate and we must not suffer ourselves to be led to adopt these analogies till some reason can be discovered for them." By that time of course the whole field of atomic and molecular weights, and of the formulae of molecules, had been revolutionised by the doctrine. Even near the end of his academic career Dalton published some essays in which he still used his old atomic weights.

Although one might say that Dalton failed to achieve all that was possible with the knowledge of his time, there is no doubt that his Atomic Theory had a massive influence on the thinking of others. His work was given early publicity and strong support by Thomas Thomson; Avogadro says he made use of Dalton's ideas given in Thomson's "System of Chemistry," published in 1807.<sup>28</sup> Thomson visited Dalton in 1804 to discuss his theory of mixed gases, and Dalton revised some of his ideas on the basis of their discussions. Thomson wrote a paper in 1813 with the title: <sup>86,87</sup> "On the Daltonian Theory of Definite Proportions in Chemical Combinations," and it contains the statement, "The opinion of Sir H. Davy that it (water) is a ternary compound of an atom of oxygen with two atoms of hydrogen, cannot, I think, be supported." So, Avogadro's work on this topic was not accepted by everyone at that time.

Thomson mentions some work that predates Dalton's by the Dublin academic William Higgins,<sup>88</sup> a man who Partington says<sup>89</sup> "did not suffer from excess of modesty." Higgins' claim that he anticipated Dalton's Atomic Theory was given support by Davy in his Bakerian lecture to the Royal Society in 1810<sup>90</sup> (Davy criticised many ideas of his "learned friend," Dalton). However, a careful reading of Higgins' publications, particularly his book "Comparative View", by Thomson and others (particularly Wheeler and Partington<sup>91</sup>), has failed to support most of his claims. Higgins' later book<sup>92</sup> is, says Partington, polemical, attacking Dalton. What is almost certainly true is that Dalton did not know of Higgins' work until it was drawn to his attention, although Davy was insistent that he did.

Jöns Berzelius is also recognised as one of the fathers of chemistry, following his publication of a text-book on the subject (in Swedish but translated into many languages) in 1808. He introduced the symbols for the chemical elements in the style we have today, he discovered several new elements, measured the atomic weights of many, and published tables of atomic weights some, optimistically, to three decimal places (his standard was oxygen as 100). He is noted in this article because of his recognition of the importance of John Dalton. In an essay published in 1814,93 he begins a section on the cause of chemical proportions with a statement of the Law of Multiple Proportions, and says that when we reflect on this, what presents itself as the most probable idea is that bodies are composed of atoms, or of molecules which combine 1 with 1, 1 with 2, etc., and as far as I know the English philosopher John Dalton was the first person to establish that hypothesis. In this article he notes the importance of Gay-Lussac's work, and almost stated Avogadro's hypothesis; at least he saw how this hypothesis would enable a table of atomic weights to be established. "It is evident that if the weight of the volumes of the elementary bodies be known, and expressed in numbers, we have nothing more to do in every case of analysis but to count the relative numbers of volumes of the constituent parts .....".

Another source of atomic weights was provided by the discovery of Dulong and Petit,94 published in 1819, that the product of the specific heat and the atomic weight of the element was a constant. Dalton discusses this law<sup>95</sup> and says in reference to a table of Dulong and Petit: "The inference intended from this table is pretty obvious, namely, that the atoms or ultimate particles of the above bodies contain or attach to themselves the same quantity of heat, or have the same capacity." Dalton notes that as the law does not hold for molecules it differs from a suggestion he made earlier that such a law would hold for all elastic fluids (gases) at the same temperature and pressure. Dalton's doubts on this matter induced him to make further specific heat measurements: "From several measurements of this kind, I am convinced that the capacity of common air for heat is very nearly such as the above ingenious French chemists have determined." He goes on to support the existence of caloric (like many others at the time), but he did not use the law to correct atomic weights, as did Berzelius, and later Cannizarro.

Our last thought on Dalton's Atomic Theory is whether he had any influence on molecular shape. We have noted earlier that he used models of balls and sticks to illustrate molecules, and Fig. 4 shows molecular shapes having a nice symmetry that would not be too far away from some that could be found in a modern text-book. But the idea that molecules have definite shapes does not appear to have been seriously considered until the work of Pasteur in 1848, and later van't Hoff and LeBel, both publishing in 1874. Kekulé, for example, writing his important paper on carbon compounds in 1858, says that radicals are not groups of atoms closely bound together but only atoms located near each other, which in certain reactions

do not separate, while in others they break apart. Kekulé's structural formulas<sup>96</sup> have none of the simplicity of Dalton's molecular symbols. So, if we were to suggest that Dalton influenced other chemists by his structures it would have to be much later when the idea of molecules having definite shapes was on much firmer ground.

## Epilogue

The details of Dalton's Atomic Theory have been superseded: we do not accept the caloric theory of heat, we know that water or ammonia are not HO or HN, we accept Avogadro's hypothesis, we explain diffusion by means of kinetic theory, we acknowledge that most elements have isotopes and we are aware that atomic fission is possible. Nevertheless, as Cardwell noted,26 we honour Dalton "because, in simple terms, he indicated the way ahead." The notion that the material world is made of atoms of definite weight and size, "which we have the power to rearrange in new ways is the master concept of our age;"<sup>97</sup> Dalton can surely justly be named as its begetter.

# Acknowledgements

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