

## Dalton's Atomic Theory: Its Origins

DALTON was not the first to suggest that matter was atomic. He had been anticipated in that over two thousand years previously, and the idea was familiar to all his contemporaries. What he did suggest was that each element had characteristic atoms, of which it might be possible to determine a most important property, namely the relative weight. Limited though this suggestion may be, its ultimate importance can hardly be exaggerated.

In previous chapters we have looked at the general progress of atomic and particulate notions up to Dalton's time, and we have seen how Dalton gradually introduced himself into the scientific world by his study of phenomena in which the degree of interest in the exact composition of substances was small. He was now to intrude into a field in which interest in the exact composition of substances was intense. The effectiveness of a new scientific theory is often dependent to a great extent on its appropriateness to the state of development of science at the time. Chemistry was ready for Dalton even if Dalton was not ready for chemistry.

On 21 October 1803 Dalton read a paper to the Manchester Literary and Philosophical Society on gas solubility which was not published until 1805. Dalton set out in it a 'Theory of the Absorption of Gases by Water', in eight sections, the last of which must be read in full: the last sentence but one is among the great utterances of modern science.

8. The greatest difficulty attending the mechanical hypothesis, arises from different gases observing different laws. Why does water not admit its bulk of every gas alike?—This question I have duly considered, and though I am not yet able to satisfy myself completely, I am nearly persuaded that the circumstance

depends upon the weight and number of the ultimate particles of the several gases: those whose particles are lightest and single being least absorbable and the others more as they increase in weight and complexity.

(Here there is a reference to a footnote which says 'Subsequent experience renders this conjecture less probable.' He goes on:)

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. The principle cannot be entered upon in this paper; but I shall just subjoin the results, as they appear to be ascertained by my experiments.

There follows a 'Table of the relative weights of the ultimate particles of gaseous and other bodies.'

That 'the principle cannot be entered upon in this paper' is about the most exasperating observation that was ever made by a historical scientist. Quite soon after, Dalton gave an explanation of the logic of his discovery, but even with this before us we are not certain even now just how he was led to it initially. The logical structure of a completed theory is often vastly different from the shape of the ideas that led to it, and in Dalton's case it is still a matter of dispute how he was led to put forward this table, the essence of which is the keystone of modern chemistry.

Dalton himself gave at least three accounts of how he arrived at his theory, which are inconsistent amongst themselves and with other information. This has become one of the favourite problems of the detective-minded amongst historians of chemistry, quite understandably, because it is very difficult to give a connected account even of the successive publications on Dalton's theory without being led aside into speculation about who suggested what, when, and why.

If the paper that Dalton read in 1803 did in fact contain most of what was in the published version of 1805, it made no impression on his audience. We can see the significance of its last page now but it can have had very little meaning to Dalton's contemporaries as it stood, since it offered only figures without real interpretation. The first useful audience

for the ideas which lay behind the figures was Thomas Thomson who visited Manchester during a tour of the north in 1804 and heard from Dalton their theoretical significance. He published an account of it in his own important textbook in 1807. Dalton's own table of figures had included only gaseous compounds. Thomson adds some figures for metals and salts, so taking the first step to relating Dalton's theory to the work on equivalents which had already been going on for a long time but still lacked a rational basis.

In 1807 Dalton himself lectured in Edinburgh and in Glasgow where he was so well received that he was moved to inscribe the first volume of his *New System of Chemical Philosophy* to the 'Professors of the Universities, and other residents, of Edinburgh and Glasgow' who had encouraged his lectures. The dedication is also addressed to the 'Members of the Literary and Philosophical Society of Manchester who have uniformly promoted his researches'. He began to write this work on his return from Scotland and in a prospectus dated 12 May 1808 announced that it was in the press and would be ready for publication in June, price seven shillings. He was able to send four copies to Dr John Bostock in Liverpool on 22 June.

The book opens with a long account of theories of heat, for which Dalton used Lavoisier's term 'caloric'. Heat is a constituent of matter and a principal factor in its organization, the most important factor being, however, the existence of particles.

The historic passage of the book is relatively brief. The chapter heading is 'On Chemical Synthesis'.

Chemical analysis and synthesis go no farther than to the separation of particles one from another, and their reunion. No new creation or destruction of matter is within the reach of chemical agency. We might as well attempt to introduce a new planet into the solar system or annihilate one already in existence, as to create or destroy a particle of hydrogen; it is one great object of this work, to shew the importance and advantage of ascertaining *the relative weights of the ultimate particles, both of simple and compound bodies, the number of simple elementary particles which constitute one compound particle, and the number of less compound particles which enter into the formation of one more compound particle.*

The next few pages cannot be denied the title of work of genius. The rules he gives are too simple to be condensed any further:

If there are two bodies, A and B, which are disposed to combine, the following is the order in which the combinations may take place, beginning with the most simple: namely,

- 1 atom of A + 1 atom of B = 1 atom of C, binary.
- 1 atom of A + 2 atoms of B = 1 atom of D, ternary.
- 2 atoms of A + 1 atom of B = 1 atom of E, ternary.
- 1 atom of A + 3 atoms of B = 1 atom of F, quaternary.
- 3 atoms of A + 1 atom of B = 1 atom of G, quaternary.

&c. &c.

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

1st. When only one combination of two bodies can be obtained, it must be presumed to be a *binary* one, unless some cause appear to the contrary.

2d. When two combinations are observed, they must be presumed to be a *binary* and a *ternary*.

3d. When three combinations are obtained, we may expect one to be a *binary*, and the other two *ternary*.

4th. When four combinations are observed, we should expect one *binary*, two *ternary*, and one *quaternary*, &c.

5th. A *binary* compound should always be specifically heavier than the mere mixture of its two ingredients.

6th. A *ternary* compound should be specifically heavier than the mixture of a binary and a simple, which would, if combined, constitute it; &c.

7th. The above rules and observations equally apply, when two bodies, such as C and D, D and E, &c. are combined.

The implications of this system are profound. All the rules of chemical proportion follow from it. The composition of any substance must be constant (Law of Constant Composition). If two elements A and B combine to form more than two compounds then the various weights of A which combine with a fixed weight of B bear a simple ratio to one another (Law of Multiple Proportions). If two elements A and B combine separately with a third element C, then the weights of A and B which combine with a fixed weight of C bear a simple ratio to each other (Law of Reciprocal Proportions or Law of Equivalents). These are modern names for these rules or laws, which

were not originally expressed with the clarity of the modern school textbook but came to be recognized somewhat gradually in these forms.

Dalton goes straight on to refer to a plate which contains 'the arbitrary marks as signs chosen to represent the several chemical elements or ultimate particles'. His signs had been in use in his notebooks for some years. Some had appeared in Thomson's textbook statement and some are to be seen on lecture diagrams used by Dalton probably in 1807. The originals perished in the fire of 1940, but fortunately the Science Museum prepared accurate facsimile reproductions (Pl. 5) of them in 1925, so that we can see them virtually as Dalton's own audience saw them.

Dalton's were not the first chemical symbols. They were not to be accepted as the agreed system of sign by chemists. The modern system familiar to everybody as  $H_2O$ ,  $CO_2$ , and so on, was devised by Berzelius, but it was Dalton who first related a symbol to an atom of element and then related that to a weight, so that the relative weight of a molecule was immediately indicated by the sum of the weights of the individual atoms composing it. Berzelius made it more convenient, but Dalton had broken the ground.

Dalton had thus by 1808 established the most important theoretical concept of modern chemistry, and had shown the way to a consistent symbolism which was eventually to be its most powerful means of communication. So excellent indeed was his pictorial system for linking questions of composition with those of structure that he felt compelled to reject the letter system of Berzelius even though he had come close to it himself. From very early on he even used solid balls to expound his theories. In his paper on 'Sugar Analysis' of 1840, he tells how his friend Peter Ewart had made them. Three only of these survive, now in the Science Museum in London (Pl. 9). They are just like the ball-and-spoke models which came into use late in the century especially after the rise of organic stereochemistry. The trouble with Dalton's symbol system was it explained too much all at once. Chemistry was not ready for a structural system, although the stoichiometric aspects of Dalton's theory were quickly used. Berzelius's letter system could handle this better than Dalton's, so it prevailed. The structural models of later years owed nothing directly to

Dalton's inspiration but it is clear that Dalton's vision was sound.

One can make these assertions about the importance of Dalton's atomism because the chemistry of the end of his century is inconceivable without it, particularly the organic chemistry with which he had comparatively little to do. The all-pervading system of chemical analysis, the demonstration by Mendeleev that the elements belonged to a consistent system, and the synthetic methods which gave unparalleled power to the chemical industry, to take only a few instances, were all directly connected with the Daltonian logic.

It is consequently a matter of the greatest interest to historians (however little consequence it may be to the practising chemist) to know how Dalton was able from the imperfect science of his day to erect a system of such penetrating possibilities. It was evident even to the earlier writers about Dalton that there was some doubt, not to say mystery, about this, and the story of the several attempts which have been made to unravel it is so interesting in itself and throws so much light on Dalton himself that I shall try to tell it here.

There have been several different explanations put forward as to how Dalton arrived at the chemical atomic theory. One can speak in two rather distinct ways of an atomic theory, and that Dalton exhibited both. One can think of a *physical* atomic theory, by which I mean a theory of the mechanical disposition of particular kinds of atoms in space, the forces which fix or change their relative position, and the properties of matter in bulk which follow. One can also think of a *chemical* atomic theory by which I mean an atomic theory of the relation between the different elements and the new substances which are formed by their union. In describing several stages in Dalton's thought as this or that physical theory or chemical theory we must not suppose that Dalton himself thought of them that way: these are terms we have adapted to try to make his mobile thoughts more intelligible.

I must also remind my non-chemical readers of the subsequent importance in chemistry of the laws of chemical composition (constant composition, multiple proportions, reciprocal proportions), and point out that logically it is as easy to derive an atomic theory from them as it is to derive

them from atomic theory, and, moreover, to anyone brought up to believe that science is based on induction, more intellectually attractive to do so: therein lies the danger that one will reverse the order of events, to make an acceptable story.

The earliest explanation to be published was that of Thomas Thomson, in his history of chemistry in 1830:

Mr Dalton informed me that the atomic theory first occurred to him during his investigations of olefiant gas and carburetted hydrogen gases, at that time imperfectly understood, and the constitution of which was first fully developed by Mr Dalton himself. It was obvious from the experiments which he made upon them, that the constituents of both were carbon and hydrogen, and nothing else. He found further, that if we reckon, the carbon in each the same, then carburetted hydrogen gas contains exactly twice as much hydrogen as olefiant gas does. This determined him to state the ratios of these constituents in numbers, and to consider the olefiant gas as a compound of one atom of carbon and one atom of hydrogen; and carburetted hydrogen of one atom of carbon and two atoms of hydrogen. The idea thus conceived was applied to carbonic oxide, water ammonia, etc., and numbers representing the atomic weights of oxygen azote, etc., deduced from the best analytical experiments which chemistry then possessed.

This would seem to have all the authority necessary: the word of the original investigator. But it was written twenty-five years later and, as was to become apparent with the discovery of Dalton's notebooks, cannot be sustained just as it stands.

The next version to be published was by W. C. Henry, author of the first considerable biography of Dalton. He reported that Dalton had said to his father, William Henry, and again to himself, that the chemical atomic theory had come to him as a result of considering Richter's tables of equivalents (see p. 234). Yet this statement was made long after the event, and the younger Henry was well aware at the time that Dalton's recollection might have been faulty. Here again we shall see that Dalton's own notebooks throw doubt on his own later assertion. (The idea is very attractive, however, and Guerlac has recently made a plea for reserve in rejecting the rôle of Richter's work in forming Dalton's ideas.) The more generally accepted version, all rest on the coming to light in

1896 of Dalton's own notebooks in the rooms of the Manchester Literary and Philosophical Society. The biographers who had written in between, notably Angus Smith and Lonsdale, had added a good deal of personal matter, but next to nothing could they add to Thomson's view that Dalton had argued inductively from examples of multiple proportions. This view was altered by the study by Henry Enfield Roscoe, one of those eminent Victorians who succeed in making a happy union of science and public service. In 1896 he published, with Arthur Harden, an account of a remarkable set of manuscripts found in the rooms of the Manchester Society and never before examined. Descriptions of other parts of this collection were published later by others but it is the Roscoe-Harden volume which is of the greatest value: of supreme value now because so large a proportion of the manuscripts themselves was destroyed in 1940.

The most striking extended passage they found was in the notes of one of the lectures Dalton gave at the Royal Institution in 1810. Dalton sketches the problem of why a mixture of gases does not separate into two layers, and refers to his theory of 1801, namely that the particles of each gas repel only their own kind. He accepts the improbability of this (e.g. the difficulty of supposing that if heat is the repulsive agent it will act differently for different gas particles) and refers to his own diffusion experiments which showed diffusion to be a much slower process than this theory would lead to.

He goes on:

Upon reconsidering this subject, it occurred to me that I had never contemplated the effect of *difference of size* in the particles of elastic fluids. By size I mean the hard particle at the centre and the atmosphere of heat taken together. And if the sizes be different, then, on the supposition that the repulsive power is heat no equilibrium can be established by particles of unequal size pressing against each other. This idea occurred to me in 1805. I soon found that the sizes of the particles of elastic fluids *must* be different.

The different *sizes* of the particles of elastic fluids must under like circumstances of temperature and pressure being once established, it became an object to determine the relative sizes and weights, together with the relative number of atoms in a

given volume. . . . Thus a train of investigation was laid for determining the *number* and *weight* of all chemical elementary principles which enter into any sort of combination one with another.

If this were all we had to go on, we could want nothing more, but in fact the order of events given by Dalton himself does not appear to agree with the notebooks he had himself written four or five years previously. He had written down some atomic weights on 6 September 1803, yet the only notes about the size hypothesis were not written until 14 September 1804. Why should he say in this lecture that the size hypothesis occurred to him in 1805 and that the idea of estimated weights occurred after that? It is true that if we did not have the evidence of the notebook entry for 1803 we might argue that the paper read in 1803 and not published until 1805 was revised in the interim in the light of the new work. After all, the atomic weight part of that paper reads very much like an afterthought.

All the same, leaving aside this puzzle of dates, the suggestion that the atomic theory grew out of a problem connected with the sizes of atoms is an attractive one when we have it in Dalton's own words, so let us set it aside to cool and look at another suggestion. In 1910-11 another student of Manchester attacked the problem, in a series of papers which have become a classic for historians of science. A. N. Meldrum examined the antecedents of the atomic theory, all the early papers, the Roscoe-Harden work, and the notebooks. He found he could 'come to no other conclusion than that it was Dalton's experiments on the combination of nitric oxide and oxygen that aroused his attention and made him apply his physical theory to the purposes of chemistry'.

These experiments were those which were described in the paper on the atmosphere read in 1802 (see p. 125) but not published until 1805. The difference in dates is once again significant. Dalton writes in the published paper:

The objects of the present essay are,

1. To determine the weight of each simple atmosphere, abstractedly; or in other words, what part of the weight of the whole compound atmosphere is due to azote; what to oxygen, etc. etc.

2. To determine the relative weights of the different gases in a given volume of atmospheric air, such as it is at the earth's surface.
3. To investigate the proportions of the gases to each other, such as they ought to be found at different elevations, above the earth's surface.

To those who consider the atmosphere as a chemical compound, these three objects are but *one*; others, who adopt my hypothesis (i.e. that the components of a mixture of gases are quite independent of each other) will see they are essentially distinct.

Dalton describes several methods of determining the amount of oxygen in a gas and recommends the one devised by Priestley, namely, reaction with nitrous gas (nitric oxide) with absorption of the soluble product. Dalton preferred this method to others (explosion with hydrogen, burning phosphorus, etc.) and describes its quantitative characteristics.

If 100 measures of common air be put to 36 of pure nitrous gas in a tube  $\frac{3}{10}$ th of an inch wide and 5 inches long, after a few minutes the whole will be reduced to 79 or 80 measures, and exhibit no signs of either oxygenous or nitrous gas.

If 100 measures of common air be admitted to 72 of nitrous gas in a wide vessel over water, such as to form a thin stratum of air, and an immediate momentary agitation be used, there will, as before be found 79 or 80 measures of pure azotic gas for a residuum.

This is very clear and obviously suggests a 2:1 ratio operating somewhere in two possible modes of combination. Dalton goes on:

If, in the last experiment, *less* than 72 measures of nitrous gas be used, there will be a residuum containing oxygenous gas; if more then some residuary nitrous gas will be found. These facts clearly point out the theory of the process: the elements of oxygen may combine with a certain portion of nitrous gas, or with twice that portion, but with no intermediate quantity.

It follows that an apparent variability of the composition of the product is due to the formation of a mixture of two substances, each of definite composition.

The ratio 2:1, argued Meldrum, suggested to Dalton a rule of multiple proportions which leads to a chemical atomic

theory—that combination is by integral units, the units being atoms. But the figures in the paper were probably obtained between 10 October and 13 November 1803, that is to say, *after* the first atomic weights of 6 September. It is true there is a note of 4 August 1803 reading, 'It appears, too that a very rapid mixture of equal parts common air and nitrous gas gives 112 or 120 residuum. Consequently that oxygen joins to nitrous gas sometimes 1.7 to 1 and at other times 3.4 to 1.' Now this reaction between nitric oxide and oxygen was nothing new. Priestley had shown thirty years previously that air reacts with nitric oxide and the reaction with oxygen was studied soon afterwards. The study of gases by measurement of volume changes had occupied Cavendish, and the term *eudiometry* was introduced in 1775. Dalton was not breaking new ground, only practising a technique, apparently new to him, for extending his exploration of a favourite problem, the composition of the atmosphere. It was known that results were apt to be variable. Chemists had put up with this for a long time but some were beginning to wonder whether nature was quite so indefinite in her behaviour as the variability of results suggested. The most articulate workers were Proust, who argued that proportions were definite, and Berthollet, who argued that proportions were variable but determined by conditions of preparation.

It is very difficult to anyone brought up in the modern tradition of chemistry dominated by small whole numbers to sympathize with the earlier chemists' constant argument about the reliability of the many values which were constantly being published for (to us) quite straightforward properties. We can accept the gradual convergence of successive determinations on a best figure. We can accept the existence of, say, two sets of values for some factor determined by two methods different in principle. But the publication of values which were the author's and no one else's, seems unhelpful to say the least. This view ignores the realities of the rough and ready world of the earlier chemist: there was no suggestion as yet to chemists that there was any more uniformity in chemical substances than there was in, say, commercial materials. Why should rock-salt be any more constant in its make-up than indigo? There was still no clearly expressible idea of purity in

chemistry, no idea that the unit of chemical thought was the unique chemical species, completely homogenous. A good deal of chemical argument already took this for granted, as for example Lavoisier's system of elements, but there was still room for a good deal of study of substances of which only a major inconstant fraction would be the species sought.

It was therefore quite possible for Dalton to find sometimes one result, sometimes another, without feeling challenged by the discrepancy. Moreover, and I think this has not been sufficiently appreciated, Berthollet's view that composition was not fixed, but was affected by physical conditions, was becoming influential just at this time. An entry in the notebook on 1 April 1803, 'Query, is not nitrous air decomposed by the rapid mixture?' is just the sort of question to be asked by someone who had not yet come down from the stoichiometric fence.

Meldrum's belief that the origin of the theory lies in the 2:1 ratio published in 1805 is therefore ill-founded, since the effective experimental work was added after the date of reading (1802).

It seems more likely that a 2:1 ratio appeared as a theory first and was then invoked to make sense of the experimental results. In the closing section of this paper Dalton criticizes Berthollet:

M. Berthollet seems to think that the lower strata of the atmosphere ought to contain more oxygen than the upper, because of the greater specific gravity of oxygenous gas, and the slight affinity of these two gases for each other. . . . As I am unable to conceive even the possibility of two gases being held together by affinity, unless their particles unite so as to form one centre of repulsion out of two or more (in which case they become *one* gas) I cannot see why rarefaction should either decrease or increase this supposed affinity.

Dalton agrees that a mixed gas might vary in proportion with altitude but the point to notice is this example of Dalton's using the union of particles as a mechanism for combination, and relating it to his theory of the repulsion of gas particles one for another. The dating of this paragraph is as indefinite as the dating of any other part of Dalton's writing at this time, but

the link of a combination theory (i.e. chemical theory) with a physical theory is plain.

We should be better able to locate the point at which Dalton conceived the chemical theory in its later form if we could tell when he got excited about it. He had been fervent enough about his auroral geometry; he cared very much for his theory of mixed gases and did his best to speed publication; he was to be vigorously controversial over Gay-Lussac's law of volumes; so he was certainly not undemonstrative. But there is no sign that he became suddenly aware of the profound character of his ideas on atomic weights. He only referred in his gas solubility paper to a principle which could not be entered upon in that paper. By his own account in the Preface to the *New System* he mentioned the atomic weight theory in the lectures he gave at the Royal Institution in December 1803 and January 1804, but writing privately much sooner after the lectures, it was on the physical parts of his lectures that he seemed most to lean for public approbation. So little, in fact, does Dalton seem to have appreciated the chemical significance of his atomic weight system that it must be considered rather unlikely that he had been thinking in chemical terms, at least of any wide generality.

We come back then to Dalton and his gases, or to be more precise, to his gases and vapours. Dalton had very long been ahead of most of his contemporaries in his appreciation of the relation between the states of matter. He was satisfied that all gases might eventually, by the exercise of sufficient and powerful experimental skill, be reduced to liquids. He was not the first to hold that a vapour and a gas are different only in degree, not in kind: Priestley had held this long before. But in the case of the controversy over the state of water in the atmosphere Dalton recognized that water vapour and the air in which it is disseminated are not intrinsically different conditions of matter. He did not hold that water either combines with or dissolves in air. In 1802 he was working on the converse system, a three-part system of gas/liquid/dissolved gas. He was in the closest communion with William Henry over this. Henry was the first to publish: in the *Philosophical Transactions* in early 1803, he gave out the relation known now as Henry's Law. At a given temperature the *volume* of gas

dissolved by a unit volume of water is independent of the pressure of the gas; this is equivalent to saying that the *weight* of the gas dissolved is proportional to the pressure. Henry had discussed this with Dalton who saw in it a link with his own studies. The behaviour of a gas dissolved in water would give information about the superincumbent gas itself, and might show whether each gas in a mixture acted independently. For some months in early 1803 Dalton worked on gas solubilities and produced a set of values which appeared to him to satisfy an elegant arithmetical relation.

If a quantity of water thus freed from air be agitated in any kind of gas, not chemically uniting with water, it will absorb its bulk of the gas, or otherwise a part of it equal to some one of the following fractions, namely,  $1/8$ ,  $1/27$ ,  $1/64$ ,  $1/125$ , etc., these being the cubes of the reciprocals of the natural numbers, 1, 2, 3, etc., or  $1/1$ ,  $1/2^3$ ,  $1/3^3$ ,  $1/4^3$ , etc., the same gas always being absorbed in the same proportion.

This, which appears early in his paper of 21 October 1803, was the last of a series of attempts to establish a formula.

The important aspect of this passage is its geometrical character. Dalton envisages a pyramid of particles, made of layers, each supporting the one above, the forces being Newtonian forces of repulsion, inversely proportional to distance. He was using the kind of image which we associate principally with the solid state, but in Dalton's mind this applied to gases just as much. When Dalton at last settled on a system to explain gas solubility it was not a matter of extracting a whole-number system out of data which only approximated to them, but rather of conceiving a geometrical explanation which could be associated only with a simple whole-number system of solubilities. The ratios quoted above are, as he shows clearly in a diagram annexed to his paper (Pl. 4), determined by the distribution of close-packed spheres. 'A particle of gas pressing on the surface of water is analogous to a single shot pressing upon a square pile of them.' He shows that a particle of gas would distribute its pressure equally amongst the pile of spheres until 'it reaches the sphere of influence of another particle of gas'. It follows, although Dalton is not explicit, that each particle is thus at the centre of a cube, the side of

which is decided by the ratio of the distance between the gas particles in the superincumbent atmosphere to that between the gas particles in the dissolved gas, that is to say each gas particle is at the centre of a cube of side of relative length 1 or 2 or 3 or 4, etc. and relative volume  $1^3$  or  $2^3$  or  $3^3$  or  $4^3$ , etc. It is implicit in this that the size of the particle of gas must be the same as the size of the particle of water, which would take some explaining, in view of the known conversion of liquids into vapours occupying considerably greater volume. But, of course, the versatile coating of heat could explain so much for Dalton and this did not yet worry him. What did worry him was the existence of more than one ratio. Why should different gases have different solubilities?

This had been borne in on him while he was collecting his figures: from the notebooks it is clear that he had figures for nitrogen, hydrogen, oxygen, nitric oxide, and carbon dioxide by August 1803. (The figure for carburetted hydrogen—methane—and probably that for olefiant gas came later, which disposes of Thomson's opinion that the atomic theory came out of the study of these gases.) The figures do show that those gases which are elements or of low density are less soluble than those which are compounds or of greater density. They might well support Dalton's belief 'that the circumstance depends on the weight and number of the ultimate particles of the several gases'.

There was one physical factor that might have given information about the relative weights of particles: the relative densities of gases. If their particles were all the same size, then the relative particle weights should have been the same as their relative vapour densities. But at least one experimental fact was against this. On page 246 of the notebook appears this:

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

In other words if A and B combine to give AB how can AB appear lighter than A? There was no reason why Dalton should

have thought of the ultimate particle of oxygen being anything other than a single atom, indeed synonymous with it. Avogadro's hypothesis, which is what Dalton was effectively talking about, was to be stated in 1811: many other than Dalton were to reject it, or misunderstand it.

What was the next simplest thing to work from? We are not at all certain that the chronology of Dalton's notes follows his pagination, but since the first atomic symbols appear on page 244, the statement above on page 246 and the first table of atomic and molecular weights appears on page 248, we can reasonably suppose that this was all in his head at the same time.

Several suggestions have been made, as I have said, about the chemical calculation which first gave Dalton an atomic weight. It seems to me that the substance which was uppermost in Dalton's mind, the characteristics of which were the key to so much else was water. He chose to reject the equal-number-equal-volume hypothesis on the basis of the composition of water. If his solubility theories were to hold together and be consistent with his theory of the atmosphere, the weight of the ultimate particle of water had to be known. The substance which had been analysed and synthesised most strikingly in the discoveries of the great generation immediately preceding him was water. Figures were available from no less an authority than the great Lavoisier. It was composed of two elements of the greatest chemical importance. It was the only compound of its elements known. I cannot show conclusively, but if I may invoke a rule of greatest simplicity in historical explanation, in emulation of my subject, I suggest that it was to water that Dalton probably first applied his own rule of simplicity, and calculated an atomic weight.

This is borne out by the 'Syllabus of a course of lectures on Natural Philosophy' dated 1805, evidently those given in Manchester in the year after his return from the lecture season at the Royal Institution. The lectures were announced in a prospectus published in 1804 which states that they were to be similar to those lately given at the Royal Institution. The order of the topics in a lecture syllabus is not necessarily the order in which these topics occurred historically, or, when they are an account of a speaker's own work, occurred to him in his



investigation. But the circumstantial evidence seems strong that Dalton thought in this order:

Lect. 15

On the Elements of Bodies and their Composition—Consideration of the divisibility of matter resumed—Assumptions, that an ultimate particle of water is composed of one of hydrogen and one of oxygen, and that one of ammoniac is formed of one of azote and one of hydrogen—reasons for the assumption—consequently that nitrous gas is composed of one of azote and one of oxygen, nitrous oxide of two azote and one oxygen, nitric acid of one azote and two oxygen, and nitrous acid of one nitric acid and one nitrous gas—Agreement of these conclusions with the phenomena—Carbon or charcoal and its combinations—

One charcoal and one oxygen—carbonic oxide.

One charcoal and two oxygen—carbonic acid.

One charcoal and one hydrogen—olefiant gas.

One charcoal and two hydrogen—carburetted hydrogen from stagnant water, etc. etc.

The solubility factors which are so closely linked with the earliest published atomic weight table are separated in this course from the atomic weight lecture: they are dealt with in Lecture 17, the syllabus for which quotes the fractions listed in the paper. The lecture syllabus was drafted probably before the paper went to press, in its final form, so we must ask why Dalton, who was proud enough of his solubility theory to give a whole lecture on the central thesis of his 1803/1805 paper, did not also write a paper of comparable length on the lines of Lecture 15. The answer must be that about this time he was faced with other demands on his energy. His lectures were very successful; in May 1805 he wrote to his brother Jonathan to say that the course was half-finished, and that 'a more respectable audience has seldom been had on a similar occasion and things have gone very well so far'. In 1806 he repeated the lectures, and on 30 November 1806 he had to write to his brother that he was very busy 'being in the midst of a Course of Lectures, and having a good deal of private tuition besides'. He had, of course, been earning his living as a teacher for most of his life, and public lectures were not new to him, but the experience of the Royal Institution evidently improved his

confidence and application so much that large-scale lecture courses now seemed to promise substantial gains, both in immediate money rewards and in prestige which would consolidate his regular teaching. The preparation of these lectures took time, effort, and investment: he had to journey to London in 1805 to equip himself with new apparatus. In 1807, no doubt with Thomas Thomson's influence, he went to Scotland to lecture in Edinburgh and Glasgow, and on his return began to write his *New System*. This was, as it were, the missing paper; the expression of those ideas which were first printed in the lecture course of 1805, held up by pressure of other business, but now demanded by both expressions of public interest and by Thomson's presentation of the theory in his own *System of Chemistry*.

Between the time of the Royal Institution lectures (the details of which remain unknown but which we may reasonably suppose were represented by the lecture of 1805) and the Scottish lectures, the source of Dalton's first chemical interpretation of atomic principles seems to have been lost to everyone's sight including his own. By the time his theory had been milled over, the original argument from the composition of water, which had received first place in his earliest surviving exposition, had retreated into the general list of examples. Water was now only one of many substances of which the composition could now be stated. As so often happens, the logical order of the textbook conceals the true historical order of discovery.