Chapter 9
Dalton's Atomism and its Creative Modification via Chemical Formulae

Abstract Dalton proposed that each element is made up of identical atoms distinctive of it and that least parts of compounds consist of characteristic combinations of small numbers of them. The laws of proportion predicted by his theory were borne out by experiment. For the first time, tentative experimental contact was made with a property of atoms, their relative weight. However, not much chemistry can be done armed only with such weights. It took a creative shift in Dalton's programme for significant progress to be made. This occurred in organic chemistry with the use of formulae and the representation of properties other than weight by suitable arrangements of symbols in them. The formulae could serve their function without interpreting the symbols in them as representing atoms. Most of the chemists involved did interpret them as representing atoms, but they differed in a crucial respect from the atoms in the philosophical tradition dating back to Democritus. The properties of atoms were to be discovered by chemical research rather than set down at the outset. The property of valency was one such property, the necessity of which became evident from the 1860s. Progress in nineteenth-century chemistry was a precondition for rather than result of the introduction of atomism into chemistry, Dalton notwithstanding.

9.1 Introduction

Our story so far has not yet reached the stage where it can be said that experimental contact with atomism has been accomplished. A plausible candidate for the first version of atomism that made such a thing possible is John Dalton's chemical atomism, formulated in the early nineteenth century. By assuming that chemical combination takes place via combining atoms Dalton drew connections between the combining weights of chemical substances in the laboratory and the weights of combining atoms. For the first time, it would appear, a line was opened to gaining some knowledge of a property of atoms, their relative combining weights.

My own view, to be developed in this chapter, is that there is much that is mistaken and misleading about seeing Dalton's atomic theory as the beginnings of an experimentally testable version of atomism. As far as chemistry is concerned, significant progress in the nineteenth-century was made, but in a way that is better

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construed as paving the way for atomism rather than resulting from it. Dalton's theory had no testable content that went beyond the laws of proportion that it entailed and so could not productively guide chemistry in a way that could not be achieved by way of the laws of proportion alone.

The situation was to change with the deployment of chemical formulae in organic chemistry. That practice was able to go beyond the consequences of the laws of proportion in a dramatically successful way. Chemical properties other than combining weight ratios were depicted by appropriate ordering of the symbols in the formulae for chemical substances. By about 1860 the demands placed on chemical formulae had resulted in a unique set of them. The arrangement of symbols in the formulae were able to capture isomerism, stereochemistry and valency, and made possible the classification and prediction of chemical reactions to the extent that it spawned a massive synthetic chemical industry. It became increasingly plausible to interpret the symbols in formulae as representing atoms, and such an interpretation was clinched by experiment around the close of the century. Dalton's own version of atomism which grew out of, and to some extent remained anchored in, physics was soon forgotten and was unproductive. The reformulation of his theory utilising formulae that made progress possible was at best a chemical atomism differing markedly from Dalton's physical atomism. There is even a case for doubting that the success of formulae in nineteenth-century chemistry represented an experimentally testable version of atomism at all. It is reasonable to argue that progress in nineteenth-century chemistry was a precondition for, rather than the result of, the incorporation of atoms into experimental science. I devote this chapter to an articulation and defence of these claims.

9.2 Dalton's Atomism

Newtonian atomists of the eighteenth century aimed to explain properties of bulk matter, such as coagulation and chemical combination, by appeal to inter-atomic forces. In the case of chemical combination the forces were referred to as affinities. A major problem with this approach was the gulf between the speculations about inter-atomic forces on the one hand and what could be investigated experimentally on the other. Near the end of the eighteenth century, Claude-Louis Berthollet, himself a Newtonian atomist, spelt out the futility of trying to derive inter-atomic affinities from experiments on chemical combination in the laboratory because an atomist must recognize that any affinities measurable at the macroscopic level are a function of the state, temperature and masses of the combining substances and arises from unknown arrangements of large numbers of atoms.[1] These problems could be supposed to be at a minimum in the case of the physical properties of gases, where an atomist could assume the atoms to be sufficiently far apart for forces of coagulation and chemical affinities to be ignored. (As it happened, the first atomic theory to gain significant empirical support, the kinetic theory of gases, made headway by ignoring inter-atomic forces altogether and admitting only the impulsive forces experienced by colliding atoms.)

Dalton's atomism emerged out of what was in key respects a Newtonian atomistic theory of gases. The details of the path that led Dalton to his theory have been much studied and debated.[2] Here I extract some of the uncontroversial features.

An atomistic theory of gases took shape in the context of one of Dalton's early research preoccupations, namely, meteorology. In 1793 we find him insisting that the absorption and precipitation of water vapour by the atmosphere is a physical rather than a chemical process. The fact that the amount of water vapour that can be absorbed by a given volume of air at a fixed temperature is independent of the pressure of the air in that volume told against the prevailing idea that the absorption was due to some chemical affinity between air and water. Dalton's understanding, atomistic from the start, was of atoms of water interspersed amongst other atoms composing air and acting independently of them. The idea that each gas in a volume makes its contribution to the total pressure independent of the other gases in the mixture was soon confirmed experimentally and has survived as 'Dalton's law of partial pressures'. Dalton developed his atomistic understanding by adapting Newton's observation, in the *Principia* (Book II, Proposition 23) that a gas made up of a static array of atoms repelling each other with a force inversely proportional to their separation will obey Boyle's law, notwithstanding the problems with this conjecture that Newton himself had already discerned.[3] Dalton speculated that the atoms of each gas repel atoms of like kind with a force inversely proportional to their separation whilst exerting no force on atoms of other gases. This explained both the law of partial pressures and also why the gases in the atmosphere remain a homogeneous mixture rather than separating out with the more dense gases settling in layers below the less dense.

Dalton soon extended his research to consider the solubility of gases in liquids, and here he was able to join forces with William Henry, who had done experimental work in the area. In particular, the latter had shown that the amount of gas absorbed in an adjacent liquid is proportional to the pressure of the gas at the liquid surface, once again suggesting a physical process rather than one involving affinities. Dalton, faced with the question of why some gases dissolve more readily in a given liquid than others, invoked the weight of the atoms of the respective gases as the likely cause of the difference. In the 1805 paper where these ideas were developed, Dalton (1805) observed:

> 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 far as they appear to be ascertained by my experiments.

Entries in Dalton's notebooks of 1803, now lost but referred to by Henry E. Roscoe and Arthur Harden (1896, pp. 26–29), imply that the atomic weights 'subjoined' to the 1805 paper were arrived at via Dalton's chemical atomism.

Alongside these studies of the behaviour of gases and integrated into them were Dalton's views on the nature of heat. His acceptance of the caloric theory of heat put him in the majority in the first decade of the nineteenth century, but what was peculiar to Dalton's treatment was the extent to which he took a strong view on the materiality of caloric and the way in which he integrated that fluid into his atomic theory. An early version of these views appeared in a five page note 'On heat', an entry in Dalton's notebook dated May 23, 1806 (Roscoe and Harden, 1896, p. 71, italics in original).

> According to this view of the subject, every atom has an atmosphere of heat around it, in the same manner as the earth or any other planet has an atmosphere of air surrounding it, which cannot certainly be said to be held by chemical affinity, but by a species of attraction of a very different kind. Every species of atoms or ultimate particles of bodies will be found to have their peculiar powers of attraction for heat, by which a greater or less quantity of heat will be conglomerated around them in like circumstances: this gives rise to what has been called the *different capacities* of bodies for heat or their *specific heat*.

Whatever its initial attraction, Dalton's efforts to pursue his physical atomism soon ran into serious trouble, and his attempts to square it with threatening experimental results had the effect of it losing whatever coherence it had. For example, Dalton's attempts to give an account of the specific heats of gases, which, as can be inferred from the quotation from Dalton reproduced above, focused on the atmospheres of caloric surrounding atoms of a gas, met with no significant support from experiment. The same can be said of Dalton's attempt to link the solubility of gases in liquids to atomic weights. There was a fundamental tension in Dalton's theory concerning the cause of the expansion of gases. The caloric theory attributed expansion of a substance to an addition of caloric, which, for an atomist, insinuated itself between atoms and pushed them further apart. Yet Dalton explained vapours in terms of 1/r repulsions between like atoms. Dalton (1810, p. 548, italics in original) did respond to this difficulty by attempting to explain the even distribution that a mixture of gases settles into by appeal to caloric. His account involved the assumption that '*every species of pure elastic fluid has its particles globular and all of a size; but that no two species agree in the size of their particles*, the pressure and temperature being the same'. The rough idea seems to be that where unlike atoms meet, there is a discontinuity in the state of caloric, because of the difference in size, and that the forces arising from this discontinuity give rise to the motions that result in the uniform mixing of the gases. It is difficult to disagree with Roscoe and Harden (1896, p. 23) when they remark that this idea 'does not appear to have been very carefully thought out, and although the conditions of equilibrium would certainly be disturbed, it is doubtful whether the intestine motion of which Dalton speaks would have been set up in a vessel filled with atoms'. Dalton expanded on his idea and illustrated it with diagrams in Part 2 of his *New system of chemical philosophy* published in 1810. Whilst these diagrams do exhibit the discontinuities arising from differing particle size, they did not help Dalton to show what he needed to show, namely, that the result of the discontinuities is a homogeneous mixture of gases and a force varying as 1/r between like atoms. It should also be noted that Dalton's assumption that the atoms of unlike substances differ in size had no independent support and Dalton himself violated the condition on a number of occasions.

Dalton's attempts to build on the early successes of his atomic theory of gases were unsuccessful. This is not surprising from a modern point of view given that Dalton worked with a static model of the arrangement of atoms in a gas and utilized a quite specific and detailed version of the caloric theory. According to an authority on the caloric theory, it does not require a modern vantage point to appreciate the shortcomings of Dalton's theory. Robert Fox (1968, p. 197) concludes an analysis and appraisal of Dalton's caloric theory with the observation that 'to his contemporaries, whether in 1800 or 1842, Dalton's work on the theory of heat must have seemed almost as wrong-headed and irrelevant to current problems as it does to us now'.

9.3 Dalton's Atomic Chemistry

Dalton's chemical atomism emerged out of his theory of gases because he saw in it the possibility of opening up an avenue for gaining experimental access to the relative weights of atoms. The bare bones of his theory appeared in the closing pages of his *New system of chemical philosophy* (1808) and can be separated from his physical atomic theory as his contemporary chemists soon learnt to do but which Dalton himself did not do.

Dalton was able to take for granted and exploit Lavoisier's chemistry and also the law of constant proportion of elements in compounds. Dalton took for granted the notion of chemical element, and the fact that the weight of each element is preserved in chemical reactions. He also took for granted the outcome of the debate between Proust and Berthollet concerning the law of constant proportions. Berthollet had likened compounds to saturated solutions, using the comparison to cast doubt on the law of constant proportions. Proust countered by establishing that the proportion of solute in a saturated solution varies with temperature whereas the proportion of elements in a compound does not, and also stressed the independence of those proportions of the method of preparation and of the physical state of the compound.[4] A third crucial component of the background, that Dalton could take for granted in a way that could not have been done half a century earlier, was the notion of gases as distinct chemicals that could be isolated, identified and weighed.

Against this background, Dalton assumed chemical elements to be composed of 'ultimate particles' or atoms that cannot be changed by 'chemical agency'.[5] The least parts of a chemical compound are assumed to be made up of atoms of the combining elements. Dalton referred to these as 'compound atoms'. According to Dalton (1808, p. 113), 'all atoms of the same substance, whether simple or compound, must necessarily be conceived to be alike in shape, weight and every other particular'. Figs. 9.1 and 9.2 show Dalton's representations of atoms and his explanation of them. The position they illustrate straightforwardly entails the law of constant proportions. The latter law already had empirical support as we have noted. But Dalton's atomic theory predicted two other laws, the law of multiple proportions and the law of equivalent proportions. The former law states that, if two

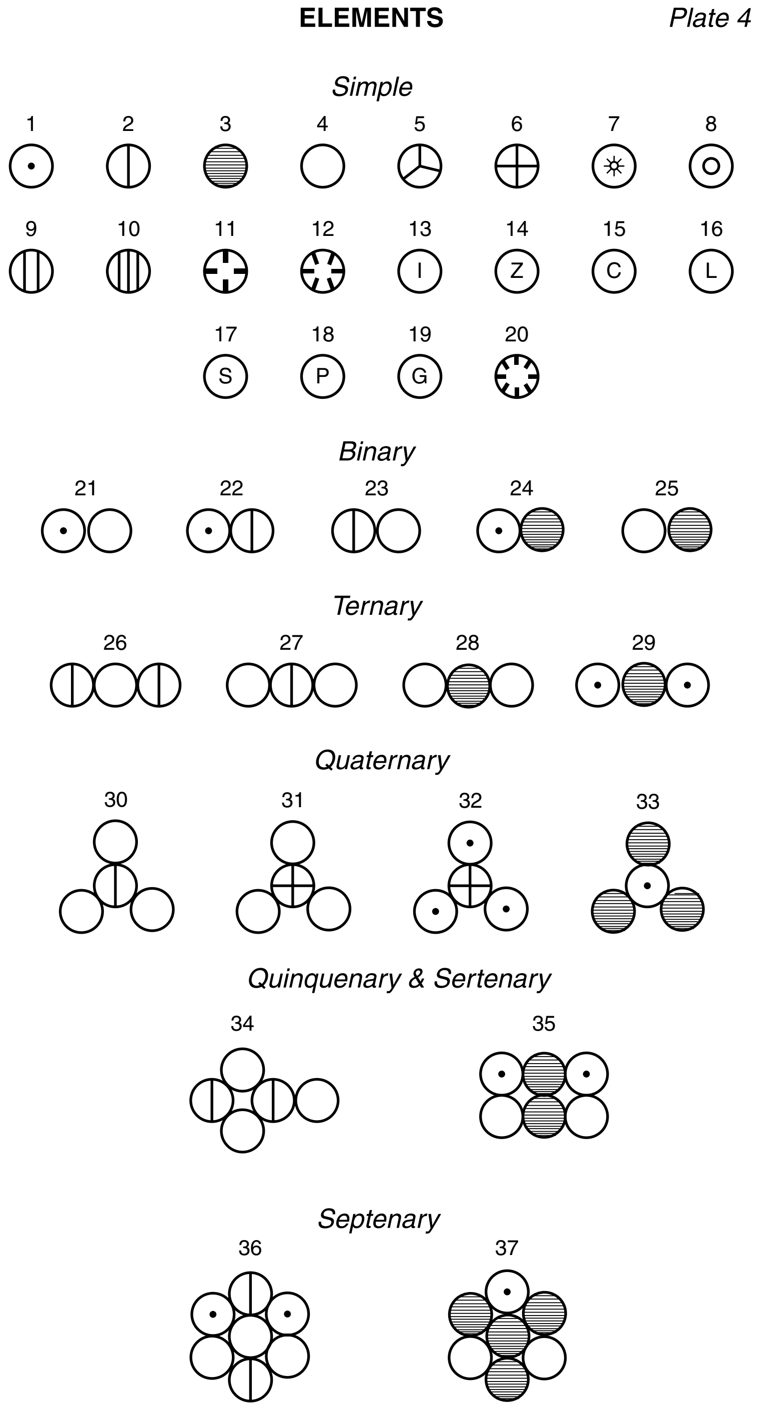

Fig. 9.1 Dalton's representations of atoms

PLATE IV. This plate contains the arbitrary marks or signs chosen to represent the several chemical elements or ultimate particles.

Fig.			Fig.		
1	Hydrog.; its rel. weight	1	11	Strontites	46
2	Azote	5	12	Barytes	68
3	Carbon or charcoal	5	13	Iron	38
4	Oxygen	7	14	Zinc	56
5	Phosphorus	9	15	Copper	56
6	Sulphur	13	16	Lead	95
7	Magnesia	20	17	Silver	100
8	Lime	23	18	Platina	100
9	Soda	28	19	Gold	140
10	Potash	42	20	Mercury	167

21.	An atom of water or steam, composed of 1 of oxygen and 1 of hydrogen, retained in physical contact by a strong affinity, and supposed to be surrounded by a common atmosphere of heat; its relative weight =	8
22.	An atom of ammonia, composed of 1 of azote and 1 of hydrogen	6
23.	An atom of nitrous gas, composed of 1 of azote and 1 of oxygen	12
24.	An atom of olefiant gas, composed of 1 of carbone and 1 of hydrogen	6
25.	An atom of carbonic oxide composed of 1 of carbone and 1 of oxygen	12
26.	An atom of nitrous oxide, 2 azote + 1 oxygen	17
27.	An atom of nitric acid, 1 azote + 2 oxygen	19
28.	An atom of carbonic acid, 1 carbone + 2 oxygen	19
29.	An atom of carburetted hydrogen, 1 carbone + 2 hydrogen	7
30.	An atom of oxynitric acid, 1 azote + 3 oxygen	26
31.	An atom of sulphuric acid, 1 sulphur + 3 oxygen	34
32.	An atom of sulphuretted hydrogen, 1 sulphur + 3 hydrogen	16
33.	An atom of alcohol, 3 carbone + 1 hydrogen	16
34.	An atom of nitrous acid, 1 nitric acid + 1 nitrous gas	31
35.	An atom of acetous acid, 2 carbone + 2 water	26
36.	An atom of nitrate of ammonia, 1 nitric acid + 1 ammonia + 1 water	33
37.	An atom of sugar, 1 alcohol + 1 carbonic acid	35

Enough has been given to show the method; it will be quite unnecessary to devise characters and combinations of them to exhibit to view in this way all the subjects that come under investigation; nor is it necessary to insist upon the accuracy of all these compounds, both in number and weight; the principle will be entered into more particularly hereafter, as far as respects the individual results.

Fig. 9.2 Dalton's explanation of his representations of atoms

chemical substances combine in more than one way to form compounds, then the ratios of the weights of one of them that combine with a fixed weight of the other are small integral numbers. (For example, the weights of nitrogen relative to a fixed weight of oxygen in the three oxides of nitrogen, nitrous oxide, nitric oxide and nitrogen peroxide, are in the ratios 4:2:1.) The law of equivalent proportions states that if weight x of substance A combines with weight y of substance B to form a compound and with weight z of substance C to form another compound, then, if B and C combine to form a compound they will do so in weights that are in the ration ny:mz where n and m are small integers. These laws were soon confirmed by a range of experimental evidence, some of it supplied by Dalton himself.[6]

Given the situation as I have described it, then, Dalton's chemical atomism was confirmed by experiments on combining proportions insofar as they supported the three laws of proportion. Three independent laws that were a natural consequence of the theory were borne out by experiment. Here I differ from Paul Needham (2004) who denies that Dalton's theory explains why chemical substances combine in constant proportions. The relationship between our respective views has some subtleties an appreciation of which illuminates the subsequent discussion of this chapter. I see no reason to doubt that Dalton's theory explains why chemical substances combine in *constant proportions*. The three laws of proportion are, after all, a straightforward and natural consequence of his theory. On the other hand, Dalton's theory does not explain why chemical substances *combine* in constant proportions. It does not explain why substances combine at all. It takes it as given. The views of Needham and myself come much closer together when it comes to the question of the prospects of developing Dalton's atomism in a direction which would take it beyond merely explaining constant proportions. Both Needham and I agree that there were no such prospects. Dalton's atomism did make contact with experiment in the arena of combining proportions. By contrast, as we have seen, the search to explain chemical combination by appeal to inter-atomic force laws had failed to engage with experiment. Was there a way of going beyond combining proportions without losing contact with experiment? As we shall see later in this chapter, there was such a way. It involved a creative transformation of Dalton's theory through the deployment of chemical formulae. It was a move that Dalton himself vehemently resisted.

As Dalton (1808, p. 163, italics in original) stressed, the 'one great object' of his new chemical philosophy was 'to show 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'*. What exactly was the 'importance and advantage' of determining such numbers? Given the form of Dalton's own version of his theory, the importance for chemistry lay in the consequences for combining proportions that followed from the numbers. However, the knowledge of combining proportions could be handled, via the laws of combining proportions and the experimental measurement of those proportions, without invoking atoms at all. Those of Dalton's contemporaries, like Humphry Davy, who identified the laws of proportion as the core of Dalton's theory and separated that from the speculative atomism had a point so long as the theory offered no prospect of moving beyond combining weight ratios.[7]

Even within the domain of combining weights, Daltonian atomism confronted a basic problem. The atomic constitution of compounds is underdetermined by measurements of combining weights of chemical substances in the laboratory. For instance, Dalton's measurement of 7 as the weight of oxygen relative to hydrogen in water is compatible with water consisting of one atom each of hydrogen and oxygen, with an atomic weight of 7 for oxygen relative to hydrogen. But it is also compatible with water consisting of two atoms of hydrogen with one of oxygen, and an atomic weight of 14 for oxygen, or with water consisting of two atoms of oxygen and one of hydrogen and an atomic weight of $3\frac{1}{2}$ for oxygen and so on.[8] Dalton had a solution to the problem that referred back to the physics underlying his theory. Since like atoms are presumed to repel each other, the most stable arrangements are those that minimise their proximity.[9] Dalton settled for one atom each of hydrogen and oxygen in water for this reason. In cases where there are multiple compounds of the same elements, Dalton suggested arrangements of atoms that maximised the separation of like atoms. So, for instance, the diagrams for nitrous oxide in the *New System* shows one oxygen atom separating the two nitrogens on either side, whilst a compound atom of alcohol (which at the time Dalton believed to be what we would write as CH_3) is depicted as a carbon atom with three hydrogen atoms arranged at 120 degree intervals around it.[10]

One problem with the simplicity rule used by Dalton to help get around the under-determination of atomic structure and atomic weights by measurements of combining weights was the question of its truth. It was not destined to be of great help to organic chemistry and, after all, it did lead Dalton to settle on one atom each of hydrogen and oxygen for water. A second problem was its insufficiency. In those cases where the same elements combined to yield more than one compound, so that no more than one of the compounds could involve the simplest arrangement of one atom of each element, the rule could not discriminate between equally simple alternatives. It could not decide, for example, which of the two common oxides of carbon is binary and which tertiary. C_2O and CO is just as simple and just as compatible with the experimental weight measurements as CO and CO_2. There were other strategies for solving the under-determination problem in Dalton's lifetime. One of them was to assume the hypothesis put forward by Avogadro in 1811 that equal volumes of gases contain equal numbers of molecules and to compare weights of molecules by comparing vapour densities. Another was to assume the law of Dulong and Petit, that the product of atomic weight and specific heat is a constant. A third assumed a correlation between atomic arrangements and crystal structure according to the 'law of isomorphism' suggested by E. Mitscherlich in 1821. The details of these attempts to determine atomic weights are sufficiently instructive to warrant a special chapter. For the moment it is sufficient for our purposes to appreciate that all of the methods involved difficulties and limitations and none of them produced definitive results. In any case, Dalton did not take advantage of them. As we shall see in 8.6, the problem of under-determination was solved, by about 1860, mainly through advances in organic chemistry made possible by use of formulae, the move that Dalton resisted.

The development of Dalton's atomic chemistry in his own hands adds weight to the charge that the content of his theory did not go beyond what can be captured by laws of proportion alone. After the publication of Volume 1, Part 1, of *A new system of chemical philosophy* in 1808, Dalton published Part 2, Volume 1 in 1810 and Volume 2 in 1827. Part 1 of a second edition of Volume 1 was published in 1842, two years before his death. This was a word for word reproduction of the 1808 edition. The chapters in Volume 1, Part 2 and in Volume 2 follow a common pattern. Beginning with simple compounds and proceeding to more complex ones, Dalton deals with their key chemical properties and their mode of preparation and then proceeds to detail the results of analysis that give the proportions of the elements in each compound. At the end of such considerations Dalton suggests an atomic constitution for the compound in question. That constitution is a result, coming at the end of the investigation. In no case does an atomic constitution guide or inform the research. This inability of Dalton's atomism to inform research in chemistry is a feature of it that will stand out more starkly when we are able, in a the following sections, to compare it with more fruitful approaches involving the deployment of chemical formulae.

9.4 The Introduction of Chemical Formulae by Berzelius

It was the Swedish chemist Jacob Berzelius who first introduced into chemistry formulae of the kind now commonplace for representing the composition of compounds. By the time he did so, in 1813, he was able to take advantage of the addition of a further experimental law that had been added to the three laws governing combining weights in 1809. That was Gay Lussac's law specifying that when gases combine at some definite temperature and pressure they do so in volumes that bear a simple ratio to each other and to the volume of the product if gaseous. Berzelius (1813, 1815) argued that using formulae was preferable to using Daltonian diagrams because the latter, in conjunction with a table of 'atomic weights', could capture all that was warranted by experiments on combining weights and volumes without commitment to the atomic hypothesis. This point is central to what follows and needs to be clarified in a way that will explain the use of italics around 'atomic weights' in the previous sentence.

An atomist will typically take the hydrogen atom as a standard so that the atomic weight of any other element will be the weight of an atom of it compared to the weight of an atom of hydrogen. From the atomic point of view, a formula of H_2O for water indicates that a compound atom of water consists of two atoms of hydrogen combined with one of oxygen. The measured equivalent weight of 8 for the amount of oxygen in water relative to hydrogen yields a relative atomic weight of 16 for oxygen. But there is no compulsion to take the weight of a hydrogen *atom* as the standard. More in keeping with what is actually done in the laboratory, any portion of hydrogen whatsoever can be taken as the standard and the 'atomic weight' of a second element can be defined relative to it. The formula H_2O will then indicate two portions of hydrogen of a given weight for a portion of oxygen that is 16 times that weight. Of course, if HO is taken as the formula for water then the atomic weight of oxygen will be 8 rather than 16. Some decision needs to be made to remove the under-determination of formulae and 'atomic' weights' by weight and volume measurements in the laboratory. But that is the case whether one is an atomist or not.

Berzelius (1815, 125–126) explained that he differed from Dalton insofar as he considered 'the atomic theory as imperfect, and as clogged with difficulties'. He promoted his introduction of formulae as an alternative to Dalton's diagrams precisely because they could be interpreted as representing combining weights and volumes without a commitment to atoms. Berzelius (1813, 359) described the view embodied in his formulae as ‘founded on something very analogous to the corpuscular hypothesis of Dalton’ but considered himself to have the advantage over the later ‘of not founding my numbers on an hypothesis, but upon a fact well known and proved’. Two years later Berzelius (1815, 127) re-iterated this point.

> I placed beside the corpuscular theory, a theory of volumes; because that theory is in some measure connected with facts that may be verified. To those who think that the theory of volumes may be fatal to the corpuscular theory, I would observe, that both are absolutely the same thing; but that the theory of volumes has this immediate advantage over the other that it may be more easily verified. . . . The only difference between the two theories consists in the words *atom* and *volume*, that is to say, in the state of aggregation of the elements.

Berzelius’s claims are problematic as they stand for it cannot at the same time be the case that his theory amounts to the same thing as Dalton’s whilst being less hypothetical. What Berzelius clearly intends is that his theory is equivalent to Dalton’s as far as the experimental evidence available at the time is concerned. That circumstance draws into question the extent to which chemical atomism can be said to be supported by that evidence.

Berzelian formulae, in conjunction with a table of relative ‘atomic weights’, can be used to represent chemical constitution without a commitment to atomism. Berzelius himself did not use this as a reason for denying atomism. Rather, he attempted to develop Dalton’s atomism further so that it would go beyond the prediction of combining weights and volumes to explain a mechanism for chemical combination. Inspired by the phenomenon of electrolysis he presumed that atoms were held together in compounds by electrostatic forces. It is doubtful whether Berzelius’s theory did have testable content in excess of the evidence for the laws of chemistry and of electrolysis that he was attempting to explain. In any case, at least in 1815, he clearly separated this hypothetical part of his theory from the account of combining weights, claiming not to attach too much significance to the former.

> I do not consider the conjectures which I hazarded on the electro-chemical polarity of the atoms as of much importance. I scarcely consider them in any other light than as an ideal speculation deriving some little probability from what we know of the chemical effects of electricity.
>
> (Berzelius,1815, p. 123).

As we have seen, Berzelius argued for his formulae as an alternative to Dalton’s diagrams on the grounds that the former can be used to express weight and volume relations involved in chemical composition without a commitment to atomism. Klein (2003, p. 20) has pointed out that those chemists who were inclined to take this path talked of combining equivalents (Wollaston), proportion (Davy), combining weight (Young), portion (Thomson) and parcel (Whewell) rather than atoms. To her list can be added doses (Donovan), combining quantities (Brande) and stoichiometrical numbers (Gmelin) as noted by Goodman (1969, p. 45). Berzelius acknowledged the hypothetical status of the atomic theory that he favoured. However, it was an hypothesis that he took seriously enough to incorporate it into his deployment of chemical formulae in organic chemistry. That deployment was to have dramatic consequences that he had not intended or anticipated, as we discuss in the next section.

9.5 The Binary Theory of Berzelius

Berzelian formulae were not much used in chemistry before the late 1820s, not even by Berzelius himself (Klein, 2003, p. 250, n. 2). This is understandable in light of the fact that, in inorganic chemistry where they were first introduced, they express little more than combining weights and volumes that can be just as well expressed in other ways. As Klein has argued in detail, this was to change when formulae were used in the much more complicated area of what is now referred to as organic chemistry. A large number of elements figure in the composition of inorganic compounds, with each compound consisting of fixed proportions of just a small number of those elements. By contrast, organic compounds are made up of a small number of elements, mainly carbon, hydrogen and oxygen and to a lesser extent nitrogen. As a consequence, knowledge of the proportions of elements in a compound is by itself an inadequate indication of its properties. In addition, a reaction involving the production of some organic substance of interest is, in organic chemistry, unavoidably accompanied by parallel reactions involving the production of by-products. In this section and the next, drawing heavily on the work of Klein (2001 and 2003) and Rocke (1984), I outline some of the ways in which order was brought to organic chemistry through the use of chemical formulae to such a degree that, by around 1860, a fairly unique set of formulae adequately characterising the properties and composition of organic compounds had emerged.

There are three features of Berzelius's chemistry that are basic to an understanding of his application of them to organic compounds. His 'binary' theory, which understands complex compounds as a combination of two less complex compounds, his electrochemical interpretation of those combinations as involving electropositive and electronegative components, and the central role that oxygen (Lavoisier's 'acidifying principle') played in his system. The idea that complex compounds have components that are themselves compounds goes back as far as the chemistry of salts, summarised in Geoffroy's table as discussed in the previous chapter, where a salt is considered as the combination of an acid and a base. Berzelius distinguished between the 'immediate constituents' of a compound into which they could readily be separated by experiment and their 'elemental' constitution, into which a compound could be divided only by a more complex series of experiments. Berzelius typically construed the immediate constituents as oxides. So, for him, copper sulphate was a combination of oxides of copper and of sulphur ($CuO + SO_3$) and sulphuric acid was a combination of water and sulphur oxide ($H_2O + SO_3$). These representations could readily be interpreted in terms of Berzelius's electrochemical theory. The pairs of immediate constituents of a compound consisted of an electropositive and electronegative component.

Berzelius was aware of the difficulties of transferring formulae to organic chemistry. One key problem that he well appreciated was the status of the law of multiple proportions in that field. That law holds that the various weights of one element that combine with some fixed weight of a second are in simple numerical ratios to each other. If those ratios are allowed to become indefinitely large, then the law loses its empirical content, because numbers can always be chosen in such a way that the law is compatible with the data.[11] The problem of reconciling the law of multiple proportions with the measured weights of carbon, hydrogen and oxygen in complex organic compounds, and of deciding on some definite integral numbers, proved to be a major one.

9.6 Chemical Formulae and the Rise of Organic Chemistry

In the 1820's a number of European chemists were less wary of applying formulae to organic chemistry than Berzelius himself had been. They employed them to display what they proposed to be the immediate constituents of organic compounds rather than simply recording their elemental constitution. Liebig, for example, represented alcohol as $C_4H_{10}O$. H_2O, which made it easy for him to regard the formation of ether (which he represented as $C_4H_{10}O$) from alcohol as involving the extraction of water. As we shall see, other chemists disagreed with Liebig and offered different formulae. In the remainder of this section I review some of the ways in which problems associated with identifying correct formulae were overcome. But one key point should be stressed. In using formulae to represent 'immediate constituents' of compounds, clearly with the intent of conveying something of chemical significance thereby, chemists were already going beyond using formulae simply to summarise what is contained in laws of combining weights and volumes.

I will not attempt to give a detailed account of, nor even summarise, the historical path that led to chemists arriving at a fairly definitive set of chemical formulae for organic compounds by the 1860s. Rocke (1984) and Klein (2003) can be consulted for those details. Here I give a schematic account of some of the demands placed on chemical formulae that were eventually to lead to a unique set of them that were able to embody chemical knowledge going way beyond laws of proportion.

One device that proved productive, exemplified in the display of 'immediate constituents' in formulae by Berzelius, involved introducing some order into the symbols representing the elements in an organic compound so that they represented properties other than mere combining weights and volumes. So-called radicals were understood as groupings of elements that remained intact through a chemical reaction and played a role similar to that of elements in inorganic chemistry. So, for instance, series of compounds could be understood as resulting from various additions to the methyl radical, CH_3, so that we have methyl alcohol, CH_3OH, methyl chloride, CH_3Cl and so on, using modern atomic weights. A fruitful idea was that of homologous series, an example of which is that involving the successive addition of CH_2 to the methyl radical to form ethyl, butyl, propyl and higher order compounds. Using this device, the properties, and even the existence and method of preparation, of higher order substances could be predicted on the basis of knowledge of the lower order ones. Berzelius introduced the terminology that distinguished 'empirical formulae', which simply indicated the proportion by weight of elements in compounds, from 'rational formulae' which included some ordering of symbols to reflect chemical properties other than combining weights. So CH_2O is the empirical formula for acetic acid whereas $C_2H_3O_2H$ is a rational formula for that acid.

The complexity of organic reactions, due to the many by-products invariably accompanying the preparation of some product, was confronted by using chemical equations to track the formation of each product. The formation of ether from alcohol by the action of sulphuric acid can be represented, using modern atomic weights, by the equation $2C_2H_6O = C_4H_{10}O + H_2O$. The numbers of occurrences of C, H and O on each side of the equation must balance, so that the weight of each element remains unchanged. Equations representing the formation of the various by-products can be represented by other balanced equations. In this way the messy process involving several parallel reactions and the formation of a mixture of products is comprehended by representing it as a superposition of identified reactions independent of each other and each represented by a balanced equation. Klein (2003, 118–129) has shown how, in the late 1820s, Jean Dumas and Polydore Boullay first used this technique to understand the formation of ether and its by-products from alcohol, thereby bringing order to a reaction that had caused confusion for decades. Thereafter, the use of chemical equations became commonplace and indispensable.

To illustrate the way in which the demands placed on formulae to adequately represent the properties of compounds and trace chemical reactions eventually led to a fairly unique set of formulae up to the task, I give examples abstracted from the historical detail.

The simplest empirical formula for acetic acid is CH_2O as pointed out above. This formula cannot be used to reflect the experimental fact that the hydrogen in acetic acid can be replaced by an equal volume of chlorine in the laboratory in four different ways yielding four distinct chemical compounds. Three of those compounds are acids similar to acetic acid and in which the relative amounts of chlorine vary as 1:2:3. The fourth compound has the properties of a salt rather than an acid. These experimental facts can be captured in a formula by doubling the numbers and rearranging the symbols in the empirical formula so that we have $C_2H_4O_2$, rearranged to read $C_2H_3O_2H$. The experimental facts can now be readily understood in terms of the substitution of chlorine for one or more of the hydrogens, with the three chloro-acetic acids represented as $C_2H_2ClO_2H$, $C_2HCl_2O_2H$ and $C_2Cl_3O_2H$ and the salt, acetyl chloride, as $C_2H_3O_2Cl$. This notion of 'substitution', which first emerged in the work of Dumas in the 1830's, where the replacement of one element or radical in a compound in the laboratory is represented by the replacement of one symbol or set of symbols by another in a formula, was to become a commonplace and powerful technique. The manipulation of formulae on paper, substituting symbols by others, could be highly suggestive of experiments to be conducted in the laboratory.[12]

The notion of substitution had a ready application in the understanding of the action of acids in terms of the substitution of hydrogen. This is already exemplified in the previous section, where the hydrogen, at the end of the formulae, responsible for the characteristically acidic behaviour of acetic acid, is separated from the other hydrogens and the formation of the salt, acetyl chloride, is represented as the substitution of chlorine for the hydrogen. It became recognised that some acids are polybasic, with two or more replaceable hydrogens and capable of forming two or more series of salts.

My third example involves Alexander Williamson's experiments with ethers published in !850. I draw heavily on Rocke (1984, pp. 215–223) but abstract from some of the chemical detail.[13] The experiments showed formulae for alcohol and ether championed both by Dumas, on the one hand, and Justus von Leibig on the other, were inadequate to accommodate his experimental results, whereas Williamson's own formulae could readily do so.

Dumas considered alcohol to be composed of the etherin radical (our ethylene) and two portions of water, and conceived of the formation of ether as the removal of one of the waters. So we have the equation

$$C_4H_8.2H_2O = C_4H_8.H_2O + H_2O$$

A corresponding formula for the formation of methyl ether would be

$$C_2H_4.2H_2O = C_2H_4.H_2O + H_2O$$

Liebig, by contrast, saw alcohol as the hydrated oxide of the ethyl radical, and once again understood the formation of ether as the extraction of water. On this view, the equations for the formation of ethyl and methyl alcohol are

$$C_4H_{10}O.H_2O = C_4H_{10}O + H_2O$$

and

$$C_2H_6O.H_2O = C_2H_6O + H_2O$$

Williamson's version of the formation of ether is represented by the equation

$$2C_2H_5OH = (C_2H_5)_2O + H_2O$$

With the corresponding equation for the formation of methyl ether

$$2CH_3OH = (CH_3)_2O + H_2O$$

Williamson's representation strongly suggests that the addition of concentrated sulphuric acid to a mixture of ethyl and methyl alcohol could yield, not only ethyl and methyl ether but a mixed ether, methyl-ethyl ether, the formation of which is represented as follows:

$$CH_3OH + C_2H_5OH = CH_3.C_2H_5O + H_2O$$

This mixed ether cannot be reconciled with the formulae of Dumas and Liebig, so the experimental preparation of that ether by Williamson told in favour of his formulae.

By the 1860s, then, formulae in organic chemistry had made possible major advances sufficient to spawn a synthetic chemical industry, and were such that formulae, and hence relative 'atomic weights', could be established. By the time this had been done it was possible to ascribe a novel property to chemical elements, namely, their valency. Armed with this notion, chemists were able to devise structural formulae for chemical compounds, as illustrated most dramatically in the work of Kekulé. Phenomena such as isomerism and optical rotation could readily be comprehended by the three-dimensional formulae built up from elements with a specific valency. The question I now raise is the extent to which this development can be considered a triumph for, and confirmation of, atomism.

9.7 Chemical Formulae a Victory for Atomism?

I have already hinted that I think there is a case for the view that nineteenth-century chemistry paved the way, rather than constituted a case, for an experimentally based and testable version of atomism. In describing the steps that led to unique formulae in organic chemistry I carefully avoided reference to atoms. The symbols in chemical formulae can of course be taken to refer to atoms. But, as we saw when discussing Berzelius's first introduction of formulae, those symbols can also be taken as referring to combining portions or volumes. On this interpretation, the structural formulae of organic chemistry depict some structure possessed by chemical compounds that is related to their chemical properties. But that structure need not be an atomic structure.

To do justice to the points I wish to make in this section I introduce a distinction between three positions that I refer to as physical atomism, chemical atomism and agnostic anti-atomism. My distinctions are related, but not identical, to those made by others, Rocke (1984) and Klein (2003) in particular.

Physical atomism involves atoms that are embedded in some physical theory such as those of the mechanical philosophers or Newton and possess physical properties such as mass, shape, size and the propensity to attract or repel other atoms. The kinds of properties possessed by physical atoms are determined in advance of chemical research by the physical theory that governs them.

Chemical atoms are the least parts of chemical elements. As well as mass, a property shared by chemical and physical atoms, chemical atoms are presumed to possess chemical properties characteristic of the elements they are atoms of. The kinds of properties it is necessary to attribute to chemical atoms is to be determined by chemical research. An example is valency, interpreted as a property of atoms by chemical atomists, which emerged in the course of advances in organic chemistry as we have seen.

Agnostic anti-atomism involves a refusal to commit to atomism. It is not a denial of atomism, which is a claim of similar strength to its affirmation. An agnostic anti-atomist would claim that the practise and success of the chemistry with which we are concerned does not require a commitment to atoms and is compatible with the idea that chemicals retain their properties however much they are divided. According to this view, the dramatic successes of the enterprise cannot straightforwardly be taken as evidence for atomism.[14]

It is clear that both a physical and a chemical atomist is free to use chemical formulae, interpreting the symbols in those formulae as representing physical and chemical atoms respectively. But an agnostic anti-atomist is free to use them too. The discussion in the previous sections of the path that led to unique rational formulae for compounds makes perfect sense if formulae are taken simply as describing chemical properties as well as combining weights and volumes. As already indicated, I deliberately omitted any reference to atoms in that section. The appearance of OH at the end of the formulae for a compound indicates that it has the properties of an alcohol, whilst CO_2H is indicative of an organic acid and so on. Further, the substitution of one element for another in a compound in the laboratory is mapped by the replacement of one symbol for another in a chemical formula. The formula of a compound represents some structure of that compound, but it does not have to be an atomic structure. The compound could possess the structure all the way down, as it were.

An analogy will help illustrate the coherence and intelligibility of agnostic-anti-atomism and its assumption that the indefinite divisibility of chemical substances is compatible with their characterisation using formulae. The electric field, $\underline{E}$, has the symmetry of an arrow whilst the magnetic field, $\underline{H}$, has the symmetry of a spinning disc. These facts led Maxwell and his followers to assume that $\underline{E}$ represents a strain in the aether whilst $\underline{H}$ represents a vortex in that aether. But there is no aether. The fields of classical electromagnetism are continuous and possess what structure they have all the way down. Agnostic anti-atomism was viable up until 1860 and beyond because no chemical evidence told against the possibility that chemical compounds possess their structure all the way down. Given the state of affairs in 1860 there was no guarantee that physical and chemical atoms would not be banished from science in the way that the aether came to be.[15]

A number of chemists involved in the developments of concern in this paper can be classified as chemical atomists. Kekulé (1867, 303–304), for example, made the distinction between physical and chemical atomism, and his commitment only to the latter, quite explicit. The historian Christoph Meinel (2004, 257) confidently invokes ‘the usual distinction between chemical and physical atoms’ which ‘provided a common denominator for those who did not want to engage in metaphysical debates about the existence of atoms, but sought to pursue chemistry pragmatically’. Chemical atomists were certainly judicious in distancing themselves from physical atomism. The gap between the abstract claims of physical atomic theories and chemical experimentation could not be bridged prior to the 1860s at least, and physical atomic theories gave no useful guidance to organic chemistry. If the rise of the latter owed a debt to Dalton at all, it was to the chemical atomism that others creatively extracted from his work, rather than to the physical atomism that he espoused.

The fact that the use of chemical formulae is compatible with agnostic anti-atomism raises the possibility that the rise of organic chemistry did not constitute a strong case for atomism at all. The productive enterprise of arranging symbols in chemical formulae to capture chemical properties other than combining weights or volumes, and the representation of the replacement of one element or group of elements in a compound in the laboratory by the replacement of one symbol or group of symbols by others in a formulae made perfect sense without a commitment to atomism as we have seen. Pierre Duhem (2002) spelt out a detailed defence of this position at the turn of the century. Many of the relevant nineteenth-century research papers invoke formulae with no mention of atoms, whilst use of the term 'atom' is dispensable in those that did invoke the term. Further, many of the chemists that did refer to atoms interpreted them as useful fictions when pressed on the matter.[16] As David Knight (1992, 120) puts it, 'chemists were almost all atomists, but recognised atomism as an optional extra' when pressed. The scepticism of many chemists concerning the existence of atoms is borne out by the 'atomic debates' that took place in Britain in the 1860s and 1870s, documented by Brock (1967). There is little doubt that, as the century progressed and as links were forged between chemistry and physical processes such as the behaviour of gases, electrolysis, optical rotation, the osmotic pressure of electrolytes and non-electrolytes, spectroscopy and so on, the case for interpreting the symbols in formulae as representing atoms became increasingly powerful. An experimental path to knowledge of atoms was eventually forged. I have raised doubts about the extent to which nineteenth-century successes in chemistry constituted such a path. To the extent that structural formulae in chemistry do signal a commitment to atomism, it was a chemical atomism that emerged out of chemical practice and owed little or nothing to the physical atomism that had a long history from Democritus to Dalton.

9.8 Dalton's Resistance to Chemical Formulae

Now that we have traced the path that led to major advances in chemistry via the use of chemical formulae, it is instructive to reconsider Dalton's chemistry in contrast to it.

Dalton's diagrams did not play the suggestive and constructive role that Berzelian formulae came to play in organic chemistry, as Klein (2003, pp. 23–40) has argued. Dalton's diagrams appear in only a few places in his work. They appear in Appendices to both parts of Volume 1 of *The New System*, they were made public in a lithograph shown at the 1835 meeting of the British Association for the Advancement of Science in Dublin, and a few of them appear in the piece 'On the phosphates and arseniates' printed in 1840. They are never used by Dalton as a heuristic aid or in any other way in the body of any of the texts. This is in stark contrast to the constructive use of formulae evident in the writings of organic chemists such as Dumas and Liebig on the Continent, and by Frankland and Williamson in Britain soon after Dalton's death. The productive use of formulae as 'paper tools' for guiding and describing the work of organic chemists in the nineteenth century is stressed by Klein (2003, p. 33) who refers to the 'graphic suggestiveness and maneuverability' of formulae as opposed to diagrams. The constructive use of formulae is as striking in the work of Dumas, for example, as is the absence of any such use of diagrams in Dalton's texts.

To some extent Dalton did employ the notion of the 'immediate constituents' as opposed to the elemental constituents of a compound, although he did not use that terminology. This was already the case in 1808 when Dalton (1808, p. 163) stressed the importance, not only of the number of 'ultimate particles of simple bodies' in a compound, but also the number of 'less compound particles which enter into the formation of more compound particles'.[17] It is also evident in Dalton's commentary on his diagrams of some atoms. For example, as can be seen from Figs. 9.1 and 9.2, diagram 34, representing nitrous acid (N_2O_3), is described by Dalton (1808, p. 164) as composed of one atom of nitric acid (NO_2) plus one of nitrous gas (NO). However, Dalton did not put the notion of immediate constituents to productive use in the way that organic chemists using formulae learnt to do. Diagram 34, in Fig. 9.1, representing an atom of nitrous acid does not of itself show two component parts, one consisting of nitrous gas and the other of nitric acid. It is only the verbal commentary on the diagram, shown in Fig. 9.2, that does that. Exactly the same diagram appears in Volume 1, Part 2 of the *New system*, but this time the text describes nitrous gas as made up of one atom of oxygen combined with two atoms of nitrous gas.[18] Plus signs, subscripts and brackets could be used to introduce structure into 'rational formulae' in a way that could not readily be done with diagrams.

My case concerning the unproductiveness of Dalton's own version of atomic chemistry stands in contrast to what a number of Dalton scholars have claimed. Arnold Thackray, for instance, talks of Dalton's chemistry being conditioned by 'a conviction of the importance of structural chemistry' and asserts that 'his views on structure possessed a power far beyond his critics' perceptions'. 'Precisely the sort of three-dimensional thinking he [Dalton] pioneered', writes Thackray (1972, pp. 117 and 124) 'was to prove vital not only to the spectacular progress of organic chemistry in the nineteenth century, but also to the triumphs of molecular biology in our own time'. W. V. Farrar (1968, p. 297), in an article on 'Dalton and Structural Chemistry' goes so far as to claim that 'if more chemists had been playing with balls and sticks in the same way as Dalton, then we would not have had to wait so long for the theory of structure', although the substance of his paper suggests an interpretation more in keeping with my own.

One of the advantages of the use of formulae in chemistry that became of increasing importance from the late 1820's on was the need to distinguish between isomers. So, for instance, methyl ether could be written as $(CH_3)_2O$ as distinct from its isomer ethyl alcohol, C_2H_5OH, with the form of these formulae immediately conveying that the first has properties typical of ethers and the latter those typical of alcohols. It is frequently claimed that the ability to deal with isomers by invoking atomic structure was one of the early triumphs of Daltonian atomism. I was certainly told so at school. The historian C. A. Russell (1968, p. 263) makes such a point quite unambiguously when he refers to isomerism as 'the first successful prediction of the atomic theory' whilst the philosopher Alexander Bird (1998, p. 152) is equally forthright in claiming that 'the phenomenon that eventually clinched the debate in its [Dalton's atomic hypothesis] favour was the ability of the theory to account for the phenomenon of isomerism, which was discovered some considerable time after Dalton proposed his view'. Dalton never used his diagrams to distinguish between isomers so far as I am aware. Nor could they be used to do so with anything like the facility of chemical formulae. But, more to the point, atomism did not and could not predict isomerism because no assumptions about the relationship between structure of atoms and chemical properties were included in its premises. Isomerism was discovered experimentally by chemical means. The results of analysis showed the existence of compounds containing the same elements in the same proportions which nevertheless had differing chemical properties. Formulae could be and were readily deployed to reflect this experimental fact in a way that could be emulated with Daltonian diagrams only with difficulty and with the aid of accompanying text. Isomers were accommodated by utilising the conventions underlying the use of formulae to represent chemical properties. This could be done in a way that did not even commit one to atomism.

The nature and status of Dalton's atomic chemistry compared with that on the Continent, the former wedded to physical atoms as represented by Daltonian diagrams and the latter making use of Berzelian formulae, was a question that became a matter of concern for the members of the British Association for the Advancement of Science. It is clear from the records of those deliberations that they sensed the fact that British chemistry was being left behind by developments on the Continent, which was certainly the case as far as organic chemistry is concerned. The *Report of the Committee on Chemical Notation*, published in the official *Report* of the meeting of the British Association in Dublin in 1835 cites a number of observations made by William Whewell, one of which expressed the recognition that most chemists in other nations had adopted Berzelian formulae and 'the only effect of our keeping back would be, to throw us behind science'.[19] Whewell's remarks also show that he was aware that use of Berzelian formulae involved less of an ontological commitment than use of Daltonian diagrams.

> Dr Dalton's method supposes a theory, Berzelius only states a fact. The notation of the Swedish chemist shows that such and so many atoms are present. Dr Dalton's, on the other hand, attempts to show their method of molecular arrangements, of which we have no positive knowledge whatsoever.[20]

Whewell was right to infer that there was a strong sense in which the use of formulae initiated by Berzelius involved less theoretical commitment than Dalton's atomism, the latter involving a fairly literal interpretation of diagrams of compound atoms. But he was wrong to imply that use of formulae involved no theory. The deployment of, and disputes concerning, rational formulae by the Continental chemists assumed low-level chemical theories, involved, for example, in the understanding of acids in terms of substitutable hydrogen, in the claims that various radicals persisted as such through a wide range of chemical change, that atoms or portions represented by the algebraic symbols could be substituted one for another and so on. The key point, not quite made by Whewell, is that the theory involved in the use of formulae was of a kind that could be tested by chemical experiments, whereas, at the time, the strong claims about atoms involved in Dalton's theory could not be.

The records of the Dublin Meeting show that Dalton strongly resisted replacement of his diagrams by formulae. He is reported as insisting that 'regard must be had to the arrangement and equilibrium of the atoms (especially elastic atoms) in every compound atom, as well as to their number and weight'.[21] Dalton had prepared a lithograph showing his illustrations of elements and compounds. He regarded his method as 'the only one representing nature'. These remarks reveal the extent of Dalton's commitment to the physical reality of his spherical atoms and the extent to which his thoughts on them were still tied up with the physical theories from which his atomism had emerged. The lack of chemical utility of Dalton's approach compared to the one involving rational formulae is starkly apparent once we focus on the organic compounds represented in Dalton's lithograph. If we replace Dalton's spheres by symbols then we get CHO for acetic acid. This leaves absolutely no scope for the quite different compounds arrived at by replacing hydrogen by chlorine either inside or outside the radical. Whether diagrams could be put to suggestive use or not, the fact is that Dalton himself put them to no such use. Two years later, in 1837, Dalton reaffirmed his opposition to Berzelian formulae.

> Berzelius's symbols are horrifying: a young student in chemistry might as soon learn Hebrew as make himself aquainted with them. They appear like a chaos of atoms. Why not put them together in some sort of order? [They] equally perplex the adepts of science, discourage the learner, as well as to cloud the beauty and simplicity of the Atomic Theory.[22]

Dalton's persistence on this point is presumably a reflection of his commitment to a physical theory of atoms, a theory which I have argued was ill-supported and unproductive during Dalton's lifetime and beyond.

One more point gives some historical support to my somewhat negative view of the productiveness of Dalton's atomism. Edward Frankland was an English chemist who had became familiar with the use of formulae in organic chemistry during a period in Germany working with Hermann Kolbe and Robert Bunsen. He did pioneering work on organo-metallic compounds. In 1851 he gave his inaugural lecture as the first professor of chemistry at Owens College, later to become the University of Manchester.[23] One might have expected him to ingratiate himself with the dignitaries of Manchester that were present by making much of John Dalton, the figure they would have been keen to claim as one of their own. In fact, Frankland made just one passing reference to Dalton, mentioning him in the same breath as William Henry. The lack of significance of Dalton's chemistry that is implied here, made public by Frankland in 1851 in Manchester, is totally explicable on the assumption that Frankland took for granted the views on Dalton I have canvassed in this chapter.

9.9 Is My Critique of Nineteenth-century Atomism Positivist?

Am I not making too much of my critique of atomism in nineteenth-century chemistry? After all, from a historical point of view most of the chemists who contributed to its advance, especially in organic chemistry, were atomists of some kind or other, the atomic interpretation of formulae gained more credibility as the century advanced and it was eventually fully vindicated. If the reader is inclined to respond to my insistence on the viability of agnostic anti-atomism in the nineteenth-century as the stance of a positivist who does not appreciate the role of theory in science, then he or she would certainly not be the first to do so. I devote this final section of the chapter to a clarification of what I see as the substance and the point of my critique.

In my analysis of seventeenth-century developments I distinguished between philosophical matter-theories, which were theories of matter in general accommodated to the phenomena, and scientific theories that were designed to explain a limited domain of phenomena and were confirmed by experiment to some significant degree. I argued that the distinction was present in practice in the work of Boyle and Newton and made explicit by them on occasions. By the nineteenth century the distinction between philosophy and science had become more pronounced and was becoming institutionalised. The term 'science' came to have its modern connotations and the term 'scientist' was introduced. In the first half of the nineteenth century Auguste Comte attempted to capture this distinction with his 'postivism'. He distinguished between mythical or theological explanation, metaphysical explanation and scientific explanation. The former predominated in the era before the philosophers of Ancient Greece replaced it by their critical metaphysics that in turn was eventually challenged by scientific knowledge based on observation and experiment. I do not endorse the details of the way in which Comte and later positivists such as Ernst Mach explicitly characterised science. It was much too narrow and unable to adequately capture the theoretical dimension of science and the ways in which it can be borne out by experiment (as opposed to mere observation). But it should be clear that I do endorse the importance of the distinction between science and philosophy or metaphysics. If this makes me a positivist then so be it.

The way in which I characterised the distinction between experimental science and philosophical matter theories in the seventeenth century needs to be modified to characterise the situation that had emerged by the early nineteenth-century. When, for instance, Laplace attempted to explain elasticity of solids by speculatively specifying inter-atomic forces he was not offering a theory of matter in general but rather of a quite specific set of phenomena. In that respect it was analogous to experimental science rather than philosophical matter theories. On the other hand, to the extent that there was no support for Laplace's atomic assumptions independent of the phenomena involving elasticity that they were designed to explain, his theory was accommodated to, rather than confirmed by experiment just like philosophical matter theories. Those chemists who objected to atomism can sometimes be read as doing so because it lacked the experimental support appropriate for a science and at other times because it constituted an inappropriate reduction of chemistry to physics. Chemists had come to see their enterprise as autonomous from physics. As we have seen, those chemists who did endorse atomism endorsed chemical atomism. The properties of atoms were to be discovered by chemical research rather than imported from some matter theory of the physicists. The property of valency, for example, posed problems for physicists' conceptions rather than being a consequence of them

Nineteenth-century chemists had every reason to be wary of importing physical atomism into their science. The time was not yet ripe for any such importation to be of any guidance to their experimental work. But I have conceded that once chemical formulae were showing their worth, most chemists were chemical atomists of some kind or other. The chemists who took a stand against atomism are best interpreted as objecting to physical, rather than chemical, atomism. The objections to atomism in chemistry generally that were articulated by Pierre Duhem were very much the exception rather than the rule. Am I, then, giving to much credence to agnostic anti-atomism as opposed to chemical atomism?

In my construal of agnostic anti-atomism I suggested that the structures exhibited by chemical formulae need not be interpreted as atomic structures. Substances could conceivably be continuous, possessing their structures all the way down. I claim that chemistry at the time of Kekulé did not involve evidence that required a chemical atomistic rather than an agnostic interpretation of formulae. There is an instructive analogous situation. By the mid-nineteenth century evidence for a wave-theory of light was considerable and the Newtonian particle theory was no longer a serious contender. But a distinction can be made between an undulatory theory of light, on the one hand, that remains agnostic on the question of what the undulations are undulations of, and a theory that attributes light to transverse waves in an elastic aether, on the other. Since the weaker assumption could stand tests against the available evidence just as well as the aether theory the question arises of what warrants the stronger assumption. Ernst Mach was one of the few nineteenth-century figures who saw things this way. In his optics he endorsed an undulatory theory but declined to attribute the undulations to oscillating states of an aether. The line of questioning with respect to the aether was stressed by Einstein around the turn of the century, at a time when the aether theory had been extended to electromagnetism and light waves were recognised as electromagnetic waves. The fact that the aether could be removed from optics and electromagnetic theory without any loss of empirical content became an argument for dispensing with the aether. A point I wish to stress is that, for most of the nineteenth century, there was no guarantee that the atom would not be banished just like the aether.

My suggestion that chemical substances might possess the structures exhibited by chemical formulae all the way down is strange and counter-intuitive. But so is the claim that electric and magnetic fields are states that have a structure but are not states of any underlying medium. Twentieth-century science was to undermine many of the intuitions that lay behind philosophical assumptions informing metaphysics. Any adequate understanding of the nature of science needs to include an appreciation of how this came about. However 'obvious' the atomic interpretation of chemical formulae may be or have been, it was not a necessary consequence of nineteenth century chemistry. In this respect I am in agreement with Pierre Duhem. In another respect I totally disagree with the French philosopher. Duhem expressed the view that knowledge of atoms was impossible in principle whereas I maintain that in the nineteenth century the case had yet to be made. Subsequent developments were to show just how wrong Duhem was. The remainder of this book shows how (after a digression in the following chapter).

Notes

1. This aspect of Berthollet's work is summarised in Thackray (1970), pp. 230–233.
2. For details see Roscoe and Harden (1896), Nash (1956), Thackray (1972), Cole (1978) and Rocke (1984, Chapter 2).
3. The assumption that atoms of a gas repel each other with forces proportional to 1/r has the consequence that the pressure of a large sample of a gas will be greater than that of a smaller sample when the density of the two samples are the same, contrary to what experiment straightforwardly shows to be the case.
4. The outcome of the debate was not as decisive at the time as it became in retrospect and it may well be that the emergence of atomism increased the attractiveness of the law of constant proportions.
5. Dalton (1808, p. 163). All quotations from this work refer to the 1964 Citadel edition.
6. The issue of whether or not Dalton was aware of the simple ratios borne out by the composition of the oxides of nitrogen and used it in the construction of his theory is a tricky one. See, for example, the discussion in Rocke (1984, pp. 29–33). Further support was soon coming, in 1808, from experimental work on the oxalates and carbonates of strontium and potassium by Thomas Thomson (1808) and William Wollaston (1808).
7. Davy made this distinction when commenting on the award of a Royal Medal to Dalton in 1826. See Knight (1967, pp. 18–20).
8. Dalton stuck to a relative atomic weight of 7 for oxygen long after experiment was well able to single out 8 as a much more accurate figure. On page 6 of a short paper 'Quantity of acids' that an ageing Dalton had printed along with sundry other pieces he wrote: 'In 1807 I first published in my system of Chemistry Part1, the atom of water; it was 1 for hydrogen and 7 for oxygen = 8, the relative weight of an atom of water. I have seen no reason for alteration from that time to this, in 1840'. In a talk delivered in 1830 he did use 8 for oxygen, 'not because I think it is the most correct, but because it is frequently met with in the books of chemistry' (Thackray, 1972, p. 98).
9. Dalton (1811) made the basis of his simplicity rule explicit in response to John Bostock's charge that it was arbitrary.
10. As a matter of fact, Dalton was not entirely consistent on this point in the *New System* as observed by Klein (2003, p. 39). The last three of Dalton's diagrams (Figure 9.1) show like atoms in contact. This inconsistency was removed in subsequent versions of the diagrams.
11. Berzelius's awareness of this problem is discussed by Klein (2003, pp. 20–23). The problem is also discussed by Maureen Christie (1994).
12. For details of the emergence of the notion of substitution, as an unintended and unanticipated consequence of Dumas's research, and for a discussion of its powerful suggestiveness see Klein (2003, 188–206).
13. Williamson did not prepare his ethers directly from the alcohols, as in my simplified scheme, but from 'ethalate of potash' (potassium ethoxide) obtained from alcohol my dissolving potassium in it.
14. My distinctions between the various kinds of atomism overlap with those made by Rocke and Klein but are not identical. The main difference lies in my distinguishing agnostic anti-atomism from chemical atomism. Rocke (1984, pp. 10–15) distinguishes between physical and chemical atomism. For him, it is the latter, rather than the former, that productively informed the rise of organic chemistry in the nineteenth century. In Rocke's view, chemical atomism

'was universally (if implicitly and often unknowingly) accepted throughout the course of the nineteenth century' whereas physical atomism 'was controversial and far from universally accepted' (p. 10). He characterises chemical atomism as affirming the existence for each element of 'a unique 'atomic weight', a chemically indivisible unit, that enters into combination with similar units of other elements in small integral multiples' (p. 12). He insists that this chemical atomism 'has greater content than stoichiometry' (p. 13). Most of this is consistent with chemical atomism and agnostic anti-atomism as I have defined them The exception is Rocke's inclusion, in his chemical atomism, of the notion of chemical atoms assumed to be 'chemically indivisible units'. My claim is that the story of the rise of organic chemistry, as Rocke himself has told it, did not require a commitment to chemical atoms and could be accommodated by an agnostic anti-atomist. Organic chemistry in the third to the sixth decades of the nineteenth owed its dramatic success to assumptions that went beyond what could be sensibly construed as generalisations from observations made in the laboratory, and certainly went beyond what is contained in the laws of proportion. The idea that the properties of organic compounds are related to an invisible structure that goes beyond weight relations and which can be mapped by rational formulae, the representation of the replacement of one element by another in a compound by the substitution of on symbol by another in a rational formula, the construal of acids in terms of replaceable hydrogen and so on were all theoretical assumptions. In light of this, I can agree with Rocke (1984, pp. 12–13, 84–87, 177–180) that those chemists, notably William Wollaston and Leopold Gmelin, who expressed themselves in terms of a definite set of equivalents rather than atomic weights, did not thereby avoid a commitment to theory. Such a commitment was necessarily involved in use of formulae to express more than combining weights and volumes. However, my position differs from Rocke's because my distinction between chemical atomism and agnostic ant-atomism allows me to deny that this theoretical commitment was necessarily a commitment to chemical atomism. An anonymous referee of a paper of mine objected to my claim that Ursula Klein's portrayal of the emergence of organic chemistry is compatible with agnostic anti-atomism. That referee interpreted Klein as defending chemical atomism in this context and invited me to read her book more closely. I have done so, and find no need to alter my original claim. Klein agrees with Rocke in claiming that the use of formulae by organic chemists went beyond what is implied by laws of proportion insofar as they were used 'to model the invisible constitution of organic substances' (2003, p. 11). The symbols in chemical formulae indicated 'scale-independent bits or portions of elements, which overlapped but [were] not identical with the concept of "atom" in the philosophical and physical tradition' (2003, p. 12) so that 'Berzelian formulas had a theoretical meaning that differed from "atomic" composition" ' (p. 14–15). The notion of a 'scale-independent bit or portion' is ambiguous. According to one interpretation, the bits or portions are discrete ontological entities which have a definite weight and any other property that they possess whatever scale one might choose to measure them by. According to a second interpretation, the bits or portions are any sample of a chemical element, however small. These bits or portions will all alike posses the chemical properties of the substances they are bits or portions of, whilst the 'atomic weights' involved in specifications of weight relations in chemical combinations and substitutions will be scale invariant because they are *relative* weights. It is the second of these interpretations that makes most sense of Klein's work. The distinction made by Klein (2003, p. 252, n. 24) between 'scale independent chemical portions' and 'particles in the micro-world' would seem to require this as does her insistence that the object of the work of the organic chemists in deploying formulae 'was not the behaviour of sub-microscopic atoms but rather, in a traditional intellectual framework, the macroscopic level of substances or substance components and their recombinations' (Klein, 2003, pp. 265–266, n. 24). In short, Klein's work on the introduction of Berzelian formulae into organic chemistry fits well with what I have termed agnostic anti-atomism.

15. This comparison is discussed in more detail in Chalmers (2008).
16. For instance, Edward Frankland, whose work helped in the formation of the concept of valency, referred to talk of atoms as 'a kind of ladder to assist the chemist' (as cited by Brock, 1967, p. 21).

17. Dalton (1808, p. 163).
18. Dalton (1810). The text is on page 366 and the diagram on p. 561.
19. Thackray (1972, p. 118).
20. *Ibid.*, p. 118.
21. *Ibid.*, p. 117. The diagrams in Dalton's lithograph are reproduced on p. 119.
22. This is from a referees report on a paper on salts by Thomas Graham cited in. Brock (1993, p. 139). Graham's paper was published in spite of Dalton's negative appraisal. It would appear that the editor of the *Philosophical Transactions* sought a second opinion, that of W. H. Pepys. The latter's report, held in the library of the Royal Society (Referees Reports, 1832–1849), recommended publication and remarked 'In respect to the chemical symbols used by the author, I have not studied them but I see they were printed in his former paper'. It would appear that the editor had specifically asked for Pepys' view of Graham's use of formulae in the light of Dalton's negative remark.
23. See Frankland (1852) for the text of the lecture.