Has Daltonian Atomism Provided Chemistry with Any Explanations?

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Philosophers frequently cite Dalton's chemical atomism, and its nineteenth century developments, as a prime example of inference to the best explanation. This was a controversial issue in its time. But the critics are dismissed as positivist-inspired anti-realists with no interest in explanation. Is this a reasonable assessment?

1. Introduction. It is often said that modern atomism in chemistry began with John Dalton, who is described as the first to go beyond purely speculative theories and put atoms to work in actually explaining chemical phenomena, notably the law of constant proportions. How reasonable a claim is this?

Faith in the power of the atom is encouraged by elementary school textbooks, which present a simple, easily visualized picture, reminiscent of Dalton's drawings. This naive picture is not borne out by what we think of as the proper way to deal with the microrealm, however, namely the application of the principles of quantum mechanics. Nor is the micro-account the whole story. Macroscopic thermodynamics is an abstract subject which chemistry students have to master at university, although it has hardly seeped down to the elementary school curriculum. But as a strictly pedagogical device, Daltonian atomism is justified as a way of approaching this more sophisticated picture, developed long after Dalton's time, which certainly can lay claim to explanatory success.

Yet philosophers remain impressed with this naive picture. Alexander Bird seems to accept the explanatory virtues of the old atomic theory, since he claims that Dalton postulated "entities which would explain the

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observable phenomenon (the law of fixed proportions)" (Bird 1998, 123), although he offers no hint of how he thinks the supposed explanation is supposed to work. Isomerism, he continues, "clinched the debate" (152) in favor of atomism without giving any sense of what the debate about the status of the atom in chemistry was about. Perhaps, like Robin Le Poidevin (2000), he puts the "refusal to engage with the structure of matter" on the part of critics of atomism down to "a view of chemistry as essentially to do with observation and experiment," imposing "an operationalist approach, [which allowed] chemistry to remain autonomous" (Le Poidevin 2000, 131). But emphasizing operationalism to the exclusion of other reasons provides a distorted perspective on the debate. The more interesting lines of argument, at any rate, either questioned whether any coherent notion of an atom had ever been formulated, or questioned whether atoms were actually given any explanatory role.

If we refrain from reading into Dalton's theory ideas which have emerged with some sort of clarity only well into the twentieth century, is there any justification for the remarks of Bird and Le Poidevin quoted above? Can we say that Dalton painted the broad strokes of an explanatory picture which in some shape or form is retained in twentieth century chemistry? For that matter, did he offer any explanation at all of constant proportions, whether or not the essentials of his theory survived into the modern period?

I will argue that he gave us no explanation at all. Though it will not be possible to pursue this story here, it seems to me that atomism began to contribute explanations of chemical phenomena much later, post-dating in large part the development of a viable non-atomic conception of the atom. Only by putting aside unjustifiable claims of explanatory worth will it be possible to trace the contribution that atomistic conceptions have really made to the development of modern chemistry and properly relate them to the explanation of chemical combination provided by thermodynamics towards the end of the nineteenth century.

2. Constant Proportions. Atomism was not new with Dalton; it has been around since the Greeks. What was it that distinguished Daltonian atomism from its predecessors which might justify its claim to being the beginning of modern chemical atomism? Whatever it was, it was certainly not enough to carry unbridled acceptance, for Dalton had many critics. The usual story, as we saw above, puts this down to positivist scepticism about what can't be seen. This is of no interest here. It is certainly not necessary to resort to positivism in order to find arguments against nineteenth century atomism; it suffices to consider the quality of the explanations on offer. The central issue, as Bird points out, was the ancient question of chemical combination, which in Dalton's time was put into a new perspective by the law of constant proportions.

The idea that compounds comprise fixed proportions of elements was familiar by the end of the eighteenth century. It was clearly presupposed by Lavoisier's analysis of the composition of water reported in 1789. The law of constant proportions was finally established by Proust against the last pocket of resistance in the form of Berthollet's objections. Berthollet compared compounds with what came to be called saturated solutions, whose composition is fixed by the circumstance of the solvent not being able to take up more of the solute. We think of zinc forming a compound by reaction with sulphuric acid, for example. But adding zinc to a beaker of sulphuric acid is like adding sugar to a beaker of water. At first, the sugar, like the zinc, disappears. But beyond a certain point, no more zinc is taken up into the liquid and it remains as a solid, just as continually adding more sugar to the water eventually leads to two phases after the power of the liquid to take up the solid has been saturated. By Berthollet's lights, the combination proceeds, with the production of a homogeneous product, in both cases until the affinities are exhausted.

Proust responded by distinguishing, amongst homogeneous mixtures, between compounds and solutions according to the preservation of composition under changing circumstances. The composition of a saturated solution is fixed only under given conditions of temperature and pressure. Once these conditions are varied, then the maximum amount of solute that can be taken up by a given solvent varies—sometimes appreciably, sometimes only slightly, depending on the substances concerned. Proust's analyses showed that compounds could be distinguished from solutions by virtue of their elemental composition remaining fixed whatever the ambient temperature and pressure, and whatever the chemical route by which they are produced. In the first years of the nineteenth century, when Proust was deemed to have emerged victorious from the dispute, the law of constant proportions rested on the analysis of only a few compounds, and the analyses of compounds forthcoming in the ensuing decades, many due to Berzelius, were regarded as substantiating Proust's claim.

Constant proportions therefore provided a criterion for distinguishing amongst homogeneous mixtures between compounds and solutions. Mere presence in a homogeneous mixture of the appropriate elements in the appropriate proportions is not sufficient for being a compound, however. Where a compound and a solution with the same composition exist, they have in general markedly different properties. At normal temperature and pressure, a mixture of hydrogen and oxygen in gravimetric proportions 1:8 is a gas, whereas the corresponding compound is liquid. And even when both compound and solution are in the gas phase at the same temperature and pressure, the former has a volume just two thirds of the latter. The state of combination of the constituent elements in a compound is thus distinguished from the state of the corresponding solution. What was therefore required of an explanation of the law of constant proportions was an explanation of chemical combination accounting for the difference between compounds and solutions.

Did Dalton respond to this challenge? Clearly, the homogeneity of compounds means that smaller quantities contain smaller amounts of the elements, although in the same proportion as in the larger quantity. But it is hardly explanatory to say that quantities of hydrogen and oxygen combine in fixed proportions by weight to form water because hydrogen and oxygen comprise smaller chunks which combine in fixed proportions by weight to form water. This merely repeats what has to be explained on a smaller scale. Not only that; it seems that it must be ultimately repeated on an invisible scale, as though taking the ultimate combining units out of sight provides the magic explanatory ingredient. Aristotle's question in *On Generation and Corruption*, "Why should indivisibility *as such* be the property of small, rather than large, bodies?" (1984, I.8, 326a27f.) receives no answer from Dalton's work. Positivism aside, if there is a complaint to be made about invisible atoms, then, it is one of obscurantism.

Nevertheless, Dalton seems to have thought the atomic hypothesis furthered our understanding of constant proportions. In a letter to Berzelius in 1812, he records that

> The doctrine of definite proportions appears to me *mysterious* unless we adopt the atomic hypothesis. It appears like the *mystical ratios* of Kepler, which Newton so happily elucidated. The prosecution of the investigation can terminate, I conceive, in nothing but the system which I adopt of particle applied to particle, as exhibited in my diagrams. (reprinted in Roscoe and Harden 1896, 159)

But the real mystery is how the general idea of atomicity is supposed to alleviate the quest for understanding. The bare fact of constant proportions implies nothing about whether such division would eventually come to an end with atoms or proceed indefinitely. It is consistent with either alternative. Some further point is needed to sway the balance.

The law of multiple proportions might be brought in at this juncture—that when the same elements combine to form several different compounds, they do so in proportions which are simple, integral multiples of one another. Dalton clearly thought that the simple relations between the alternative proportions into which the same elements combined spoke in favor of atomism. There doesn't seem to be any immediate reason why, on a continuous theory of matter, multiple proportions should stand in such simple, integral relations. On the other hand, there is no reason why, in the absence of any account of combination, continuous matter shouldn't have discrete features. After all, discrete features arise from continuously varying magnitudes in the quantum mechanical explanation of chemical bonding. Moreover, since Dalton's atoms had spatial parts just as do larger chunks of matter, the question why extended matter of some chemical kind should be indivisible given that larger portions of the same kind of matter are counts directly against the atomic theory. It is difficult to see that multiple proportions raises a greater problem for continuous matter than indivisibility raises for atoms.

This brings us back to the question of what the explanatory point could be of postulating minimal amounts of elements, of relative size such as to maintain the elemental proportions at this atomic level. Mere repetition of the proportions seen on the macroscopic scale is clearly no explanation; some relevant, independent property of the atoms must be involved. Dalton was led to postulate such a feature when arriving at his law of partial pressures. He applied the idea in the explanation of constant proportions, but in so doing he failed, I shall argue, to meet the challenge.

3. Dalton's Account of Chemical Combination. Combining proportions were supposed to be the ratio of the sums of the weights of all the atoms of each element in any given quantity of the compound, and thus reduce to the ratio of the sums of weights of atoms of different kinds in the molecule or minimal unit of the compound. But combining proportions don't yield atomic weights (relative to hydrogen, say) without recourse to the number of atoms of each elemental kind in the minimal unit of the compound. For this purpose, Dalton introduced an assumption, called the "rule of greatest simplicity", according to which one atom of each element is to be found in the unit. Lavoisier's determination of the composition of water as 85% oxygen and 15% hydrogen, for example, led Dalton to conclude that oxygen atoms are $5\frac{2}{3}$ the weight of hydrogen atoms, assuming in effect a binary formula, HO.

The phenomenon of multiple proportions exacerbates the problem. Carbon and oxygen combine in different proportions to form what is now called carbon monoxide and carbon dioxide, for example, and there are several oxides of nitrogen. So the assumption can't hold in general. Dalton sought to accommodate multiple proportions with a principle succinctly formulated by Thomas Thomson in his 1807 *System of Chemistry*, written after Dalton's Edinburgh lectures, which runs:

> When two elements unite to form a third substance, it is to be presumed that *one* atom of one joins to *one* atom of the other, unless . . . more than one compound is formed by the combination of two elements, [when] the next simple combination must, he supposes, arise

> from the union of *one* atom of the one with *two* atoms of the other. (quoted in Thackray 1966, 36)

But there is no telling which of the various binary compounds of the same elements has a binary unit, which a ternary unit, and so on. The atomic idea threw no light on the relation between compounds of the same elements.

Contemporaries of Dalton, such as Wollaston and Bostock, raised the obvious objection of arbitrariness. Realizing something must be said about the nature of these atoms which would explain their postulated behavior, Dalton responded with a suggestion about how atoms pack together. Assuming all atoms are spheres of the same size, he calculated that a maximum of twelve such spheres can pack around a given sphere. Importing the idea he postulated in connection with his law of partial pressures, that atoms of the same kind repel one another, the packing would be more stable the fewer atoms of a given kind pack around a given atom of another kind. A binary water molecule would minimize the internal repulsion and therefore be the most stable.

Putting aside the question whether this account is compatible with the claim that atomism explains multiple proportions, let us pursue Dalton's rationale for introducing this notion of repulsion. Dalton arrived at his law of partial pressures by the following line of reasoning. After the discovery that air was not, as Aristotle had thought, an element but contained both oxygen and nitrogen, a problem arose about its homogeneity. Oxygen is denser than nitrogen. Why, then, haven't they separated? The fact that air is a homogeneous mixture led many of Dalton's contemporaries, including his ally in the atomic debate, Thomas Thomson, to conclude "we must therefore consider air as a chemical compound" (Partington 1962, 776). But Dalton himself maintained that the dissolution of one substance in another is "purely a mechanical effect", occasioning "no need to bring in chemical affinity" (Partington 1962, 773). Dalton proposed that what he thought of as the purely mechanical mixing of the constituents of air be explained on the basis of an atomic theory in which like atoms *repel* one another. The idea of repelling atoms came from Newton's corpuscular model from which Boyle's laws could be deduced. Dalton added to this the distinctly chemical idea that, corresponding to the different kinds of elemental substances, there are distinct kinds of atoms, rather than conceiving atoms with Boyle as subunits of the minimum amount of an element. This allowed for the restriction that only like atoms repel. The mutual repulsion of oxygen by oxygen atoms, and nitrogen by nitrogen atoms, neatly explained their intermingling, suggesting how each substance strives to fill the available volume as though the other were not present. Each would exert a partial pressure totalling to the overall pressure of the air, which is just the law of partial pressures which Dalton was able to confirm in application to other cases, such as the fixed vapor pressure of water regardless of the presence of other gases.

Dalton's conception of atoms distinguished by elemental kind with like repelling like was thus conceived as the basis of a theory of solution—a state he clearly and explicitly distinguished from that of chemical combination. It was useful in leading to the formulation of the law of partial pressures. Whether his explanation can be said to be an ancestor of the modern explanation of ideal solutions is another matter.[1] But leaving that aside, the question here is whether Dalton can be said to have offered any explanation of constant proportions.

His theory offers an explanation of chemical combination only in so far as it offers an account of the stability of packing structures. Since he wasn't able to deploy this notion of stability in the case of multiple proportions to determine which of those compounds formed from the same elements be assigned the simplest unit, its contribution was in any case slight. Whatever its virtues, however, the suggestion is based on exactly the same principle that he used to explain the stability of air—i.e. of homogeneous solutions. So Dalton simply did not rise to the challenge of explaining the difference between compounds and solutions, which is the nub of the Berthollet-Proust controversy. It was already apparent to Dalton's contemporary critics, Berzelius in particular, that Dalton offered no account of chemical *affinity*. But it is the concept of affinity that is the enduring notion that chemists of all ages have grappled with in trying to understand the state of combination of elements persisting in compounds. It is difficult to identify any contribution of Dalton's in the contemporary understanding of this issue.

This is the major criticism of the claim that Dalton explained constant proportions. He developed a theory of the state of solution, and not of the state of combination. Other criticisms naturally arise once we ask about the source of the repulsion. Dalton put it down to caloric surrounding his atoms. A general "explanation" of the Charles/Guy-Lussac gas law at the time was that heating transfers to a gas caloric which, in virtue of its assumed elastic and internally repulsive nature, was supposed to explain the expansion. Bringing Dalton's use of this general idea to light hardly improves his putative explanation of constant proportions, however. For one thing, it is odd that what is supposed to be an atomic

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[1] The modern understanding of mixing doesn't rely on molecular repulsion. "It is often said that solubility is due to the molecular forces. That this is incorrect may be seen from the fact that two gases mix in all proportions and have infinite mutual solubility; the mixing is due, not to any interaction, but to the motion of the molecules" (Denbigh 1981, 244).

theory has to resort immediately to the characteristics of a continuous substance like caloric to do whatever explanatory work needs to be done in describing how the postulated explanatory entities act. Second, there is the problem that Dalton requires that only atoms of the same substance repel one another, which is a difficulty if the behavior of a single substance, caloric, is to carry the explanatory burden of repulsion for all kinds of atoms. It is presumably in the interests of countering such an objection that he resorts to caloric sticks radiating out from his atoms, which are somehow different for different kinds of atoms. Apart from being ad hoc, it is difficult even to see how it works. Judging from his diagrams,[2] there's no difficulty in getting like atoms to approach more closely. They happen to have been drawn with the tips of the caloric sticks of like atoms touching, but from those very same drawings it seems that this is a very special orientation. Keeping one nitrogen fixed and rotating the other would enable it to come closer in exactly the same way as it is envisaged that a hydrogen atom can get closer. Moreover, whatever repulsion effect the rays have seems to rely on the assumption that they are quite rigid, which is not easy to understand. How can a substance like caloric which was supposed to be light or even weightless be rigid? Shouldn't an atomic theory offer an atomic account of rigidity anyway? In any case, surely the rays are integral parts of the atoms. So why should having spikes touching as in the diagram of adjacent nitrogen atoms not amount to atoms "being together" rather than repelling one another? If this doesn't convince, then perhaps the consideration that all the elements should be acidic because of the spikes does.

4. Chemical Formulas. Dalton's pictures were superseded by chemical formulas, which are presented in modern textbooks as though they too rely on atomic notions. But atomism is not essential to the use and interpretation of the nineteenth century applications of chemical formulas, and critics of atomism from this period were certainly not obliged to abandon formulas. Basic compositional formulas reexpress gravimetric proportions by a scaling which reflects the chemical measure of amount of matter. The formulas H_2O and H_2S, for example, express that, different gravimetric proportions notwithstanding, just as much hydrogen combines with oxygen in water as combines with sulphur in hydrogen sulphide. The unit of measurement governing relations of containing just as much, twice as much, and so forth, is the chemical equivalent. Cannizzaro appealed to Avogadro's principle in resolving conflicts over chemical formulas at the famous Karlsruhe conference in 1860, which might be taken

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[2] Dalton's original diagrams in *A New System of Chemical Philosophy*, Pt. 2, are reproduced in Roscoe and Harden (1986, 22–23) and in Partington (1962, 779).

to vindicate Dalton. Cannizzaro's molecular weights are not weights of molecules, however, but dimensionless numbers expressing a relation between the substance in question and hydrogen. The formulas express proportions of elements in compounds as ratios of integral numbers of atomic (equivalent) weights—again not weights of atoms but dimensionless numbers. These numbers might be thought of as numbers of atoms in a molecule. But they are at bottom proportions, and needn't be interpreted atomistically. The Avogadro principle could be interpreted as saying that equal volumes of gases at the same temperature and pressure contain the same number of equivalents.

So far from clinching the debate in favor of atomism, as Bird claims, isomerism was accommodated by a natural extension of the principles governing compositional formulas. This can't be spelled out in the space available here.[3] But notions of valency are captured as well on this understanding of formulas as that based on the atomic theory. Here it is clear that there is no pretence of providing any explanation of valency, but merely a systematization of the number of equivalents of an element that combine with a given element in a given compound. Atomism had no more to say about valency until the electron was successfully incorporated into the picture. The interesting question is when the spatial structure which the atomic theory ascribed to molecules was first put to explanatory work and providing evidence in favor of the atomic theory.

5. Conclusion.

Acceptance of the law of constant proportions required a distinction amongst homogeneous mixtures between solutions and compounds. Dalton clearly accepted this, and offered an explanation of the former, at least for mixtures in the gas phase, leading to his law of partial pressures. But the putative explanation of constant proportions characteristic of compounds provided by his atomic hypothesis was vitiated by circularity, appealing to precisely the same feature in atoms that was supposed to be explained in macroscopic quantities of matter. This objection might be circumvented by the incorporation of some independent features of atoms in some useful way. But Dalton offers no account of what draws unlike atoms together in molecules in what would naturally be thought of as an atomic explanation of combination. Rather, he imports the basic explanatory idea from his theory of solutions to provide an account of the most stable structure in line with the arbitrary convention of his "rule of greatest simplicity." No issues are resolved by this

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[3] Duhem ([1902] 2002) gives a careful reconstruction of the understanding of structural formulas which doesn't presuppose atomism. See Needham 1996 for a shorter exposition.

unilluminating theory, which has nothing to say about what is distinctive about the state of combination.

Another tradition sought to explain the state of combination as a state of greater stability compared with others in terms of the distinction between exothermic and endothermic reactions. These ideas were criticized and corrected with the application of thermodynamics to chemical matters towards the end of the nineteenth century, providing the first explanatory account of chemical combination to be actually retained in modern theory. The account has since been further elaborated, and complemented with atomic, or at least microphysical, theories. It is unclear whether these can be said to be specifically continuous with Dalton's theory as distinct from other ideas associated with the atomic tradition since the Greeks.

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