

## When did atoms begin to do any explanatory work in chemistry?

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*Abstract:* During the 19th-century atomism was a controversial issue in chemistry. It is an oversimplification to dismiss the critics' arguments as all falling under the general positivist view that what can't be seen can't be. 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 ever really given any explanatory role. At what point, and for what reasons, did atomistic hypotheses begin to explain anything in chemistry? It is argued that 19th-century atomic accounts of constant proportions and isomerism had little to offer, whereas a nonatomic explanation of chemical combination was developed. Not until the turn of the century did atomism begin to do serious explanatory work in chemistry.

### 1. Introduction

In his 1902 textbook, *The Elements of Physical Chemistry*, Harry Jones introduces the atomic theory right from the start, associating it with the move of chemistry from a purely qualitative to a quantitative science at the end of the 18th century when investigations led to the law of constant proportions. Having just got his story under way, however, Jones feels the need to warn the reader that although "the conservation of mass is sometimes referred to as the law of the conservation of matter," the former expression "is greatly to be preferred ... since it states just what we have established by experiment. The latter goes far beyond the facts and, as Ostwald has pointed out, is pure theory" (Jones 1902, p. 2). Such caution is soon thrown to the wind when Jones attributes the "scientific atomic theory," as distinct from "older imaginative speculations about atoms and molecules," to John Dalton as "the only rational explanation of the laws of multiple proportion and combining weights" (Jones 1902, p. 4). He goes on to mention some speculations about the nature of atoms and adumbrate the evidence, such as it was, for the picture, to which I will return in section 6. What Jones passes over without comment is the fact that the basis for atomic speculation in chemistry was a controversial matter which had hardly been settled by the time he was writing. Other scientists were more consistent in maintaining a prudent reserve in the

face of inadequate evidence which might be thought more worthy of the title “scientific” than Daltonian atomism

Long after Dalton had introduced his atomic account of the laws of constant and multiple proportions at the beginning of the 19th century, opponents were describing atomism as a crutch to thinking about chemical matters by introducing pictures which could be misleading and should be dispensed with. Notoriously, when awarding Dalton the Royal Society’s medal in 1826, Humphrey Davy pointedly omitted Dalton’s atomic theory from what he considered of value. After mentioning several names involved in the history of the law of constant proportions, he says

But let the merit of discovery be bestowed wherever it is due; and Mr. Dalton will be still pre-eminent in the history of the theory of definite proportions. He first laid down, clearly and numerically, the doctrine of multiples; and endeavoured to express, by simple numbers, the weights of the bodies believed to be elementary. His first views, from their boldness and peculiarity, met with but little attention; but they were discussed and supported by Drs. Thomson and Wollaston; and the table of chemical equivalents of this last gentleman, separates the practical part of the doctrine from the atomic or hypothetical part, and is worthy of the profound views and philosophical acumen and accuracy of the celebrated author. (Davy 1840, pp. 96–7)

Although there were others who followed in Dalton’s footsteps throughout the century, atomism remained a controversial issue. Not before the first years of the new century, with Perrin’s and Einstein’s work on Brownian motion, did opposition to the existence of a world of microparticles finally disappear. Even then, Brownian motion was not directly relevant to the central questions of chemistry, and pointing to what is the generally accepted turning point in the received status of the atom doesn’t answer the question of when atomism began to do any explanatory work in chemistry.

This will not be accepted by those who think that Dalton’s atomism does explain the law of constant proportions, and came into its own with the discovery of isomerism in the third decade of the 19th century. But they must take account of the fact that even at the end of the century, several prominent scientists maintained the antiatomist stance, and it seems to me that Pierre Duhem, in particular, is substantially right in saying that the concepts of constant proportions and isomerism in 19th-century chemistry were not sufficient to motivate atomism. I shall support this position by elaborating two of his lines of argument.

Commentators sometimes suggest that it was a failure on Duhem’s part not to have more clearly acknowledged the mounting evidence for the existence of microparticles around the turn of the century. But without a fair account of what explanatory theory of atomic combination they think he should have considered, the force of this criticism

remains unclear. In retrospect, Thomson's early electron-ring model, Bohr's 1913 model, and so on, may all be regarded as valuable in so far as they heralded the new non-atomic notion of the atom—the divisible atom. These formed a series in which successive modifications eventually yielded a viable conception, free from the blatant internal difficulties afflicting these earlier ideas, and suggesting for the first time how atoms actually combine. But unless science is to be regarded as the art of seeing into the future, such post factum justification can hardly be used to fault judgements made at a given time. The explanatory adequacy of naive atomism has, in fact, always been subject to question, and if it has been redeemed by wave mechanics after 1925, this was not so much by rebuffing the old criticisms as by showing how to modify the doctrine to avoid the criticisms. Duhem didn't live to see the development of modern quantum theory, and what he opposed was the naive atomism. He might be faulted for holding too high a standard of explanatory power for the acceptance of theories; but his stand, if somewhat extreme, was not an unreasonable one. At all events, it should be clear that what is at issue is not a retrospective assessment of the contribution of Daltonian atomism to how we now know the story developed. The concern is with Dalton as scientist rather than soothsayer, and the discussion will focus on the explanatory qualities of what was on offer at the time.

When, if not at the beginning of the 19th century, did atomism start to contribute any real explanations to chemistry? This is a complicated issue, all the relevant threads of which cannot be considered here. The two themes which are pursued would suggest moving this time forward to the beginning of the 20th century; but broadening the scope of the investigation would no doubt make any idea of a definite turning point unrealistic. What is important is the issues about explanation that emerge.

Such thoughts raise the question of how continuity in the atomic tradition is to be understood. It is an important issue for that brand of realism which “typically defend[s] a cumulative approach to science,” as Stathis Psillos puts it in his recent book (1999, p. 280). The problem for such realists is to provide an account of theoretical terms which allows for the preservation of reference over a period of theory change in which many descriptions previously held to be applicable give way to new descriptions. In his own favoured approach to the issue, Psillos distinguishes two cases: where the terms themselves are retained and where they are abandoned. Whilst terms like “ether,” “caloric” and “phlogiston” belong to the latter category, presumably “atom” belongs to the former. And in dealing with retained terms, he follows Berent Eng in making the key notion that of an explanatory mechanism, the retention of which is to provide the central criterion for preservation of reference. A “core causal description” of the explanatory mechanism characterises entities of a given kind, and entities not satisfying this core description are not the same kind of entity (Psillos 1999, pp. 295–6). But if

the 19th-century opponents of Daltonian atomism were correct in maintaining that it failed to provide any adequate explanation of chemical phenomena, then there is no core explanatory mechanism to be described. By Psillos' criterion, then, reference would not be preserved and there is no continuity of the atomic tradition in chemistry.

## 2. Dalton and the Law of Constant Proportions

In his recent textbook, Alexander Bird seeks to illustrate the contentions of scientific realism by trotting out the familiar line that the value of Dalton's hypothesis lies in postulating "entities which would explain the observable phenomenon (the law of fixed proportions)" (1998, p. 123). Bird is right to say that explanation is what is at issue, and that the justification for believing in atoms hangs on the possibility of fabricating viable explanations of phenomena which stand the test of time. The unobservability of atoms was as irrelevant for the interesting opponents of atomism, and Duhem in particular, as they were to Dalton and his followers. Let us begin, then, by considering the nature of the phenomena whose explanation is at issue.

The law of definite or constant proportions, which all parties agreed was the basis of compositional formulas, doesn't confine the elements concerned to combination in only one set of proportions; there is also a law of multiple proportions. It makes composition—the proportion of its constituent elements—a necessary feature of any *compound*. Composition alone is not sufficient for being a particular compound (e.g. nitric as opposed to nitrous oxide), but only when a state of combination obtains (as opposed to a mere mixture of oxygen and nitrogen in the appropriate proportions). Although the law is often ascribed to Joseph Proust in 1799, it is clearly presupposed by earlier work, such as Lavoisier's determination of the composition of water. Duhem elucidates the significance of the law by describing the conception that Proust opposed in the final controversy. His opponent, Claude Berthollet, compared compounds with what came to be distinguished, after acceptance of the law, as saturated solutions, along the following lines:

The quantity of potash that can neutralise a given quantity of sulphuric acid is determinate. In the same way, the quantity of saltpetre or sea salt that a given quantity of water can dissolve is determinate. For Berthollet as for all his predecessors, for Stahl as well as for Macquer, these two phenomena were of the same order and should be explained by the same sort of reasoning. ... If some circumstance were to change—if, for example, the temperature were to rise or fall—the various forces would be modified and, consequently, the state of equilibrium into which they had led the system would no longer be the same as it was before the change. ... Perhaps it might happen in certain cases that a given mass of alkali always seems to neutralise the same quantity of acid, just as the quantity of sea salt

dissolved by a given mass of water depends only slightly on the temperature. But these are special cases, due to propitious circumstances, and one should be wary of taking them as distinctive of a general law. (Duhem 1899, pp. 218–9)

Proust rebuffed all such ideas by showing that the elemental composition of a compound is fixed independently of temperature and pressure, and remains a feature of the compound whatever its manner of production and under whatever conditions the compound can be said to exist. Speaking of constant, or fixed, proportions brings out this point very clearly, and for this reason may be preferred to the term “definite proportions.”

Notions of simplicity of the proportions, propounded in the light of Daltonian ideas about the packing of equal-sized atoms as their source, seem extraneous to the fundamental idea. The discovery of homologous series of hydrocarbons sufficed to quell such thoughts.

What contribution did Dalton’s atomic theory make to the understanding of Proust’s principle? So far from explaining constant proportions, Dalton’s indivisible atoms merely repeat on a smaller scale the macroscopically determined proportions—larger chunks of hydrogen and oxygen combine in constant proportions because, on his account, they comprise smaller chunks which do so. Duhem doesn’t himself compare the repetition on the smaller scale of constant proportions on the larger scale with Molière’s well-known ploy in so many words. But in his discussion of primary qualities in Part II of *Aim and Structure* he points out that the ploy backfires on the Cartesians and the atomists when they brought it to bear in criticism of Scholastic science, which “does not have a sad monopoly of these faults, for we find them as well among the followers of schools that pride themselves on reducing everything to quantity” (1954, p. 122).<sup>1</sup> No one with a sound mind could, for example, attempt to explain light by attributing it “to a virtue of brightening, to luminous corpuscles, or to a luminary motion” by advocating an Aristotelian, an atomist or a Cartesian theory, respectively, because he would not have “added a particle to our knowledge concerning light” (1954, pp. 123–4). Duhem must have viewed the attempt to explain the combination of substances by the combination of atoms without any independent account of what the combination of atoms amounts to in the same light.

Dalton was not, apparently, entirely insensitive to the charge of vacuity, and ventured some further elucidation. But his only contribution to the question of how the character of the atoms leads to the observed proportions was in terms of how spheres of

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<sup>1</sup> I argue in Needham (2002b) that for purposes of describing the history of ideas on the nature of mixts (homogeneous mixtures), Duhem puts the Cartesians and the atomists in the same camp.

the same size can pack around a given sphere. He calculated that a maximum of 12 such spheres could pack around a given sphere. Assuming atoms of the same kind of substance *repel* one another (in accordance with Newton's corpuscular model from which Boyle's law could be deduced), a collection of such spheres will be more stable the fewer atoms of a given kind pack around a single atom of another kind. Dalton imported this assumption from his explanation of the homogeneity of air, which had led him to his law of partial pressures. The problem there arose with the realisation that air is not a single substance, as homogeneity had been taken to indicate, but a mixture of oxygen and nitrogen. Oxygen is in fact denser than nitrogen. Why, then, haven't they separated? The tendency to repel one another which Dalton ascribes to atoms *of the same kind* seemed to provide the explanation required. At all events, it led him to formulate his law of partial pressures, which found independent experimental support of the same kind supporting the ideal gas laws—i.e. the law of partial pressures is obeyed by ideal gases.

Diatomic molecules of elements, impossible on Dalton's scheme, proved to be an embarrassment later. At the time, the major achievement of the law of constant proportions, as explained above, was to provide a criterion distinguishing compounds from solutions. What was therefore required of an explanation of the law of constant proportions was an explanation of the *difference* between compounds and solutions, Dalton regarding solution as "purely a mechanical effect" (quoted by Partington 1962, p. 773). Since the homogeneous mixture of air is an example of a solution, however, it was hardly appropriate to appeal to a feature held to explain the character of solutions in explaining the character of compounds. An explanation of chemical *affinity* distinguishing compounds from solutions is what was needed. It was apparent to Dalton's contemporaries who engaged in the discussion, such as Berzelius,<sup>2</sup> that Dalton's atomism didn't have the makings of a theory of *combination*. In the same spirit, Brush (1983, p. 34) points out that the modern view of valency doesn't accept that the geometry of packing explains why the chemical attractive force is "used up" when just some specific small number of atoms of another kind becomes attached, but seeks to reverse the order of explanation. In fact, the subsequently discovered counterexamples to the constant proportions criterion of compoundhood provided by interstitial "compounds" are understood by explaining how it is possible that "the ratio

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<sup>2</sup> "... when we treat atoms in a chemical theory, we ought to endeavour to find out the cause of the *affinity* of these atoms. We ought to endeavour to combine researches respecting the cause why atoms *combine* with researches into the cause why they combine only in certain proportions" (Berzelius 1815, p. 123; my emphasis).

of the number of molecules of one component to the number of molecules of the other is fixed even though it is not the result of chemical affinity between the components” (Timmermans 1963, p. 30). Given the absence of even a speculation about combination—the specifically chemical aspect of the general problem of cohesion of matter which has been discussed since Aristotle—which in atomic terms wasn’t addressed until well into the 20th century, early 19th-century scepticism towards Dalton’s contribution to the solution of the problem appears quite reasonable.<sup>3</sup>

Note that such putative explanations are not advanced by evidence for the mere existence of atoms. If the contribution of the atomic theory to chemistry is the illumination of the central question of what constitutes chemical combination, then this cannot be antedated the time when some reasonable idea of how atoms combine first emerged. Wurtz’s notion of atomicities, which Duhem discusses in section VII of his 1892 paper, might be considered a gesture in this direction. But Duhem effectively shows it to be completely *ad hoc*, providing no more insight into what an atomicity of an atom is than Molière’s doctor was able to provide about the dormitive character of opium.<sup>4</sup> The universally acknowledged evidence for the existence of microscopic particles provided by Perrin’s studies of Brownian motion around 1905 may have inspired speculation, but gave no direct clue about how atoms combine. Much the same can be said, as we will see, of Pasteur’s argument that the preservation of optical activity in solutions, which quartz loses when dissolved or fused, indicates a dependence on structure at the microlevel (Lowry 1935, p. 27).

### 3. An Explanation of Chemical Combination

Duhem was not simply offering a disinterested critique. He had his own ideas about where to look for an explanation of chemical combination. Chemical reactions form part of a broader class of physical processes which either absorb or evolve heat. Duhem (1900, pp. 17–8) considered views on the connection of heat and chemical reactions to fall into three periods. First, Lavoisier and Laplace maintained that all exothermic reactions (releasing heat) are combinations, whereas endothermic reactions are decompositions. Apparent exceptions to the latter were explained by saying that decompositions are accompanied by combinations releasing a greater amount of heat than the decomposition in fact absorbs. This theory gave way in mid-19th century to thermochemistry, proposed by Julius Thomsen and adopted by Marcelin Berthelot, according to which only exothermic reactions occur spontaneously (at a given temperature and pressure). The third theory is the one Duhem advocated in his first

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<sup>3</sup> This account of Dalton is further elaborated in Needham (2004).

<sup>4</sup> The central point is summarised in Needham (1998, pp. 54–5).

book, on thermodynamic potentials, generally taken to be his ill-fated first doctoral thesis of 1884.<sup>5</sup> It is clear from the introduction that his central topic is the problem of chemical combination. There he describes the failings of Thomsen's theory as formulated in Berthelot's principle of maximum work, which entails that "of two conceivable reactions, the one the inverse of the other, and releasing heat while the other absorbs heat, the first alone is possible" (Duhem 1886, p. ii). It could only be saved by what Duhem held to be an illegitimate demarcation between chemical phenomena, alone subject to the law, and changes of physical state which Berthelot held to be exempt from the law.

Thomsen's principle can be understood to derive from the first law of thermodynamics, which introduces the concept of energy, and the principle that equilibrium is achieved by realising the state of lowest energy. Demonstrating that a mechanical system has achieved a state of minimum energy is a recognised form of explanation in mechanics. But thermodynamic considerations presented in Gibbs' groundbreaking paper from 1875-8 show that equilibrium cannot in general be identified with a state of minimum energy. A system doesn't attain equilibrium by minimising energy *simpliciter*, but under the condition that the entropy is constant. Chemical processes are not ordinarily conducted under conditions of constant entropy, however, and Duhem developed the idea of thermodynamic potentials which Massieu and Gibbs had introduced to describe the requisites for equilibrium under conditions more readily encountered in the laboratory. Under conditions of constant temperature and pressure reaction proceeds spontaneously if the change in the Gibbs free energy,  $\Delta G$ , given by

$$(1) \quad \Delta G = \Delta H - T\Delta S,$$

is negative. A negative change in enthalpy,  $\Delta H$ , corresponding to an exothermic reaction, contributes to a negative  $\Delta G$ . But a positive  $\Delta H$  might be offset by a sufficiently large increase in entropy,  $\Delta S$ , showing that endothermic reactions are possible.<sup>6</sup> Achieving the relevantly most stable state is naturally regarded as

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<sup>5</sup> Jaki (1984, pp. 50–3) argues that this thesis must be identical with Duhem (1886).

<sup>6</sup> Note that  $\Delta S$  is not necessarily positive under isothermal conditions; the principle that equilibrium corresponds to an entropy maximum holds under the condition that the energy is constant, whereas what is now under consideration are conditions of constant temperature and pressure. Duhem warns of drawing erroneous consequences if the restriction is not observed. "It is quite certain, for example, that the entropy of a mass of water decreases when it is vaporises at constant temperature" (1887, p. 164).

explanatory here as it is in mechanics. In the 1880s, the thermodynamic account was the only explanation of chemical combination on offer.

On the question of what has been retained from the 19th century, it is important to appreciate that the unquestionable role microstructure acquired in 20th-century chemistry has not usurped the thermodynamic account. To illustrate, a standard textbook introduction to the general idea of enzyme catalysis (Elliott and Elliott 1997, pp. 1–7) stresses that enhancing the rate of reaction is only possible for those reactions which are thermodynamically possible in the sense that the free energy for the overall change is negative. Thermodynamics may have nothing to say about chemical kinetics, but kinetic variations can only operate within thermodynamically determined limits. Again, the necessity of constant proportions is no longer accepted, and the composition of the berthollides such as titanium hydride are understood in terms of (1):

A whole range of uniform materials may be formed ranging from (say)  $\text{TiH}_{0.1}$  to  $\text{TiH}_{1.8}$  in overall composition (the limits depend on temperature).  $\text{TiH}$  has no special stability, but simply represents the stage where half the tetrahedral sites are occupied at random. At  $\text{TiH}_{1.8}$ , no metal phase remains, but 10% of the sites are empty. ... Since the defect structure has a higher entropy, if a lower enthalpy, the stable equilibrium composition may not be the stoichiometric one. (Mackay *et al.* 1996, p. 93).

Combination is no longer contrasted with mere mixture as Proust insisted around 1800. The law of constant proportions had focused attention on compounds as the proper subject of chemistry. But interest in solutions was rekindled in mid-century, and Duhem (1902, p. 175) was not alone in arguing for the difficulty of drawing an absolutely general and clear distinction between solutions and compounds, even if his contemporaries didn't all appeal to thermodynamic considerations.

Whether Dalton's conception of a solution as not involving combination finds some analogue in the modern notion of an ideal solution is doubtful; it makes no appeal to molecular repulsion. From the thermodynamic point of view, formation of an ideal solution is driven entirely by the entropy of mixing, and the enthalpy of ideal solution formation in (1) is put at zero. This is far from a true picture of real solutions, and particularly so with aqueous solutions where entropy changes may be low or even oppose the solution of ionic or polar solutes, and the mixing is driven by the enthalpy factor. Heat of solution was one of several features inspiring some chemists to return to Berthollet's idea of solutions as combinations. In the 1880s Armstrong and Pickering suggested this association is driven by a "residual affinity" over and above the usual valencies of the atomic constituents of molecules (Partington 1964, p. 642), and doubted that aqueous solutions "were to be explained in purely physical terms" (Dolby 1976, p. 301). An acrimonious debate developed between the ionists and adherents of

the combination idea, feelings running high as members of the latter camp objected to omission of their criticisms in expositions of the ionic theory by the Ostwald school. Dolby expresses some sympathy with the charge that the differences “were not to be settled by rational exchange” (1976, p. 395) or in terms of what “best survived exposure to experimental test” (1976, p. 392). But he also acknowledges that the belief that the properties of solutions resulted from association rather than dissociation never led to a clear alternative theory with definite positive proposals which the Ostwald school could compare with their own. It was based on an intuitive conception of the atomic theory which would have perpetuated the gulf between chemistry and physics were the interest in developing clearly formulated laws and making their restrictions as far as possible explicit not to have flourished within the discipline of physical chemistry after Ostwald. Dolby notes that few of the early physical chemists played a pioneering role in developing the “new understanding of the atom,” suggesting (1976, p. 392) this might be connected with Ostwald’s opposition to atomism. I suggest it has more to do with the lack of direct bearing of the new discoveries on the central questions of chemistry. Radioactivity and Brownian motion were not obviously connected with chemical combination; and putting the electron to coherent and systematic chemical use took, as we will see, quite some time.

#### **4. Explanation and Deduction**

Duhem has a reputation for being a stickler for rigor. His sensitivity to the deductive order of a theory made him very much aware of the frequent failure of subsumption of phenomena under general laws to fully satisfy the requirements of strict deduction, and the need to resort to approximations at every turn. But there is no reason to think that he was critical of the necessity of giving an argument from basic principles when providing an explanation, as are some latter-day critics of Hempel’s covering law model. How else would it be possible to speak, as he sometimes does, of the bearing of remote consequences of a theory (1898, p. 55; 1902, pp. 168f.) on application and testing? Even where approximations are employed, assessment of an explanation often involves the assessment of an argument on which it is based. So much the better where approximations are not at issue and a clean deduction is possible.

Duhem readily conceded that “as Dalton showed, it is easy to deduce the fundamental laws of chemistry” (1892, p. 442). From the idea that molecules of a given kind always comprise the same numbers of atoms of specified kinds, the laws of definite and multiple proportions follow, as well as Mitscherlich’s law of isomorphism. To go beyond these primary laws and deal with isomerism and the phenomena leading to the elaboration of compositional formulas with the development of structural formulas requires that Dalton’s scheme be complemented with additional features. This

is the point at which Duhem disposes of the device of projecting valency onto atoms in the guise of atomicities. But even restricting the issue to compositional formulas, it is clear that Duhem thought that Dalton's atomism provided no explanation of the underlying laws although it entailed them.

The idea that deducibility of the explanandum from the putative explanans is not sufficient for adequate explanation is no stranger to the discussion of scientific explanation since Duhem's time. Asymmetries, illustrated by Bromberger's flagpole case, and irrelevance, illustrated by Salmon's hexed salt and male consumer of birth-control pills, provide counterexamples. Hempel himself pointed out that a law can be deduced from its conjunction with any other law. Deduction from general principles may well always be possible; as Norman Campbell once put it,

Any fool can invent a logically satisfactory theory to explain any law. There is as a matter of fact no satisfactory physical theory which explains the variation of the resistance of a metal with temperature. It took me about a quarter of an hour to elaborate the theory given on p. 123; and yet it is, I maintain, formally as satisfactory as any theory in physics. If nothing but this were required we should never lack theories to explain our laws ... It is never difficult to find a theory which will explain laws logically; what is difficult is to find one which will explain them logically and at the same time display the requisite analogy. (Campbell 1920, pp. 129–30)

Clearly, by "will explain" Campbell means "from which can be deduced"; for his point is that mere deduction is not sufficient for explanation. The point might be put in terms of candidate explanation, to the effect that Campbell's trivial theory *proposes* to explain the variation of resistance with temperature, although this is no improvement on the bare statement of the phenomenon.

An explanatory theory has to be one that we accept. But rather than grounding acceptance, with Campbell, in analogy with what is familiar, Duhem requires that acceptable explanations fall back on acceptable truths. This is the general tenor of his questioning of the scientific relevance of impeccable deduction in *German Science* when it doesn't proceed from true premises. He clearly took Thomson's admission that "Although the molecular constitution of solids supposed ... in our model *is not to be accepted as true in nature*" to undermine the claim that "a mechanical model of this kind is undoubtedly very instructive" (quoted by Duhem 1954, p. 75; his emphasis) and cast doubt on the explanatory claim of the mechanical model.

Pickering appealed to this same distinction between validity and soundness of argument when criticising the ionists' theory of solution, maintaining it was hardly "more than a mathematical exercise" (quoted by Dolby 1976, p. 383) once the analogies suggested by "the wide ranging experience of the chemist," as Dolby puts it, are

disregarded. Claiming access to truth on the basis of intuition steeped in unique experience had limited appeal, however, and came to be seen as a sign of being out of touch with new developments. There has to be some more articulate and publicly accessible reason for regarding the leading principles of a putative explanation as true.

The fact that general principles offer the possibility of explaining phenomena is itself an argument in favour of counting them true. “Pickering’s criticism of circularity” (Dolby 1976, p. 361) missed the point. The ionists engaged in thermodynamic reasoning, not to prove the theory, but to claim that the detailed manner in which it accommodates many aspects of the phenomena speaks in favour of the theory. This is the strategy, so much admired by Duhem, which Newton adopted in defending his law of gravitation against the *a priori* dictates of the Cartesians about what provides a basis for understanding. In Newton’s case, many diverse phenomena were brought under the rule of a single theory which was alone in offering such systematic explanation; and the same could be said of thermodynamics. On the other hand, a theory whose only merit is that it subsumes a particular phenomenon with a simple, unedifying argument, without forging new links with other phenomena, has little to recommend it. Employing a trivial device like that in Campbell’s example, or blatant repetition barely concealed under new terminology, offers no hope of a more general account and has even less to recommend it. It comes as no surprise that such theories have competitors accomplishing exactly the same job, and so are “underdetermined” by the phenomena. But the simple-minded idea of the hypothetico-deductive model, that implications of the truth always lend support to a theory, is restricted by the requirement of explanation.

## 5. Stereoisomerism

Bird claims that isomerism “clinched the debate” (1998, p. 152) in favour of atomism. But those who couldn’t see any explanation of constant proportions in Daltonian atomism naturally found it equally unilluminating as the basis of understanding isomerism when this came to light some three decades into the 19th century. Dalton’s pictures had been replaced by compositional formulas introduced by Berzelius in 1813, which abstracted from the spatial features of Dalton’s representation,<sup>7</sup> and the question

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<sup>7</sup> Klein (2001) argues that use of formulas to represent chemical reactions provided a quasi-algebraic medium freeing representation of substances from the restrictions of Dalton’s concrete models and allowing for the development of new possibilities, such as Dumas’ conception of substitution. In fact, as Klein points out (note 19), some of Dalton’s pictures were misleading in so far as they break his own principles of repulsion.

was whether structural formulas, subsequently devised to distinguish isomers, must be understood as a return to pictures of atoms in molecules. Duhem (1902, pp. 89–121) presented a particularly clear formulation of the atomic view of formulas. Adapting the theory of types, he construed compounds as the result of substitution of equivalents of elements or groups in an archetypal substance, and structural formulas, several of which might be compatible with a single compositional formula, displayed the different kinds of chemical reactions that isomers would enter into. These reactions were related to the number of structural formulas corresponding to a given compositional formula, which was to correspond to the number of isomers. Körner's confirmation of Kekulé's closed ring formula for benzene, for example, proceeded by showing that there are just three di-bromobenzenes, whose structures were in turn assigned on the basis that the ortho-form yields just two nitro-derivatives, the meta-form three and the para-form one. These results could be accommodated on the atomic conception of structural formulas which correctly delimit the number of different isomers.<sup>8</sup>

Duhem was by no means alone. While some chemists dithered with a distinction between chemical and physical atoms, Planck and Gibbs held outright "that entropy was irreconcilable with the existence of atoms" (Kragh and Weininger 1996, p. 108), and other chemists found it easy to resist the assumption that structural formulas pictured ultimate molecular constituents of compounds. This may seem particularly surprising after stereoisomerism entered the scene in the middle of the 19th century and the topological ordering in structural formulas was strengthened with what Duhem (1902, p. 128) described as "a new element taken from geometry."<sup>9</sup> Surely the tetrahedral structures suggested by Van 't Hoff in 1874, and thought to mark no difference in chemical properties, displayed a three-dimensional molecular structure with the appropriate asymmetries to explain the particular differences of optical isomers.

(Differences in chemical properties eventually came to light. In 1894, Fischer discovered that emulsin, an enzyme prepared from bitter almonds, hydrolyses methyl  $\beta$ -D-glucoside to methanol and D-glucose, but does not affect the  $\alpha$  form. But such chemical differences presented no problem for representation by structural formulas without the atomic interpretation. It might be added that before absolute configuration was determined by X-ray analysis, structures were assigned relative to a standard, dextrorotatory glyceraldehyde, which was arbitrarily assigned the structure of D-(+)-

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<sup>8</sup> See Needham (1996) for a summary of Duhem's account of chemical formulas.

<sup>9</sup> Note that structural formulas without this extra element, which Duhem (1902, p. 126) described with Leibniz' term *analysis situs*, shouldn't be described as two-dimensional (cf. Lowry 1935, p. 42).

glyceraldehyde. Here “(+)” indicates direction of rotation (dextrorotatory) and “D” the actual configuration about the asymmetric carbon atom. Note also that direction of rotation provided no help in assigning absolute configuration. Dissolving dextrorotatory lactic acid in aqueous sodium hydroxide, for example, yields a solution of sodium lactate which is laevorotatory, although the configuration about the asymmetric carbon is unaffected by loss of the ionisable hydrogen.)

But did Van 't Hoff's tetrahedral hypothesis explain optical activity? A difference in representation is postulated to correlate with a difference in laevo- and dextrorotatory isomers. The idea of a simple correlation is more accurately captured in Le Bel's formulation of the stereochemical hypothesis. His first principle is to the effect that, given a compound with formula  $MA_4$ , substituting three of the A's by different monovalent radicals yields an asymmetric body with rotatory power (accommodating optically active compounds without an asymmetric carbon, such as allenes).<sup>10</sup> But does mere correlation amount to explanation?<sup>11</sup> It certainly didn't satisfy Duhem. As with Dalton, there is no disputing that the existence of two isomers, corresponding to the optical isomers, is deducible from the suggested extension of Dalton's theory. But this is like the deduction of constant proportions and the “explanation” of the variation of resistance with temperature in Campbell's example. Nothing is said to motivate the specifically atomistic interpretation of the chemical formulas. Duhem complained that “van 't Hoff nowhere ... gives the stereochemical representations for the simple symbols” (1900, p. 17), i.e. of the atoms at the centre and apexes of the tetrahedron. In particular, no information is given which would indicate how plane polarised light can interact with stereoisomers so as to rotate the plane of polarisation in opposite directions. Duhem formulates Van 't Hoff's hypothesis as a correlation in two laws jointly asserting that compounds are optical isomers iff they can be stereochemically represented by non-superimposable formulas (Duhem 1902, p. 130). Arguing that a style of formulas is required to represent the exact number of isomers—which wasn't in dispute—is not necessarily to argue for features of the spatial structure of molecules.

Robin Le Poidevin (2000), like Alexander Bird a philosopher who thinks of 19th-century atomism as explaining isomerism, dwells on the explanation of optical isomerism by the 3-dimensional asymmetric carbon atom. He puts the “refusal to engage with the structure of matter” on the part of critics of atomism down to “a view

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<sup>10</sup> Snelders points out that “a regular tetrahedral structure ... was not his starting point as it was for Van 't Hoff” (1975b, p. 68), and Woolley says “it was not necessary for him to interpret [chemical formulae] as concrete microscopic material objects as van 't Hoff had done” (1982, p. 2).

<sup>11</sup> A similar question is raised by Causey (1972, pp. 414–5).

of chemistry as essentially to do with observation and experiment,” imposing “an operationalist approach, [which allowed] chemistry to remain autonomous” (2000, p. 131). Surely autonomy was promoted by the atomists who, like Kekulé (Snelders 1975a, pp. 60–1), obscured their claim by insisting on a distinction between chemical and physical atoms. But the convenient myth that opposition to atomism was entirely based on a positivist obsession with observation, rather than on a challenge to the explanatory claims of 19th-century atomism, is an obstacle to really engaging with the issue.<sup>12</sup> A more balanced view of what made the conception of chemistry as an autonomous discipline untenable would certainly require a recognition of this challenge. The union with physics which brought about the establishment of physical chemistry at the end of the 19th century is a complex issue. But as already indicated in the last two sections, it had as much, if not more, to do with innovations from thermodynamics than atomic speculation. And Duhem’s argument against Berthelot’s defence of the principle of maximum work was precisely that it rendered the autonomy of chemistry completely *ad hoc*. Putting such general issues aside, however, what atomic mechanisms were actually on offer which could provide the basis of an explanation of how molecules can interact with plane polarised light and bring about the rotation characteristic of optical isomers?

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<sup>12</sup> Ramberg (2000, §4) also says that Van ’t Hoff’s hypothesis “served to explain the appearance of optical activity” as well as number of isomers. The force of the explanatory claim is considerably weakened, however, when he goes on to say that organic chemists reasoned “by excluding questions about the actual reality of atoms from their discussion, and simply proceeding to use them as if they existed.” The claim is repeated in his recent book, where he says that “the tetrahedron as the explanation for optical activity—seems to have been accepted without any controversy at all, as there was little or no opposition to it. ... chemists offered no alternatives to the tetrahedral carbon atom for the explanation of the optical activity of organic compounds after 1874. This was either because most chemists accepted the asymmetric carbon atom as the explanation for optical activity, or because Van ’t Hoff’s general correlation between structure and optical activity could be accepted without necessarily adopting the tetrahedron.” (Ramberg 2003, p. 330). But correlations stand in need of explanation and are not themselves explanations. On Ramberg’s use of “explanation,” it doesn’t seem that this amounts to a denial of the claim in the text that Van ’t Hoff’s hypothesis didn’t explain optical rotation. The view that chemistry can only be reconciled with physics by reduction, as Ramberg says in the conclusion of his paper, would be disputed by several recent writers in the philosophy of chemistry, and it was certainly not Duhem’s view.

A quantum mechanical approach to the problem actually “showing how the rotatory power depends on molecular structure” (Kauzmann *et al.* 1940, p. 340) was developed in the 1930s. Describing the theory in the final chapter of his 1957 textbook, Walter Kauzmann makes comparisons with a classical theory expounded in his preceding chapter, which provides a general treatment of the interaction of molecules with electromagnetic radiation based on the tenets of Lorentz’s theory of electrons. The classical theory yields many equations which are preserved in the quantum theory and therefore merely require a reinterpretation, and has the distinct pedagogical advantage of providing “an understandable physical explanation of the optical properties of matter” (Kauzmann 1957, p. 547). If this is where to look for the first formulation of a mechanism explaining the systematically differing interactions of optical isomers with plane polarised light, however, then the story goes no further back than the turn of the century, when Lorentz developed his theories after the discovery of the electron in 1897. So even if the explanatory account could be said to be getting off the ground around the time of Duhem’s later criticisms, it comes a quarter of a century after the tetrahedral carbon hypothesis was put forward by Van ’t Hoff. This gulf of time effectively separates the tetrahedral hypothesis from the rudimentary explanatory mechanism.

On Lorentz’s general picture, atoms are supposed to comprise a massive diffuse cloud of positive charge within which the electrons are able to oscillate in simple harmonic motion. The specific classical model on which Kauzmann builds the explanation of rotatory power has two electrons each constrained to move along its own helical path, the two helices being of the same dimensions and intertwined along a common axis with the electrons constrained to be always diametrically opposite across this axis. Although rather artificial, it “illustrates the essential feature of electronic motion responsible for optical rotatory power,” namely “the movement of electronic charge along crooked pathways under the influence of light within the molecule” (Kauzmann 1957, p. 623), and allows Kauzmann to present a qualitative description of the lines along which the theory might be applied to 2-bromobutane (1957, pp. 634–5). Fresnel had already shown in the 1820s that the rotation of plane polarised light observed in the preceding decade could be attributed to inverse helical movements of charge in the refracting medium, anticipating, as Lowry (1935, pp. 20, 342) says, Bragg’s determination by X-ray analysis of the spiral arrangement of oxygen and silicon atoms in quartz. A feasible theory of electrons in molecules was needed to supply the connecting link with Van ’t Hoff’s tetrahedral molecular structure. The basic feature of the mechanism Kauzmann describes is the oscillation of electrons as the varying electric and magnetic fields of the incident light induce them to move along their helical paths under a restoring force obeying Hooke’s law. A steady state in which

the electrons oscillate at constant amplitude obtains after a suitable time, producing oscillating magnetic and electric dipole moments giving rise to scattered rays whose fields combine vectorially with those of the incident light and rotate it right or left according as the helices are right- or left-handed. The strengths of these moments are inversely proportional to the difference between the square of the natural frequency of the electron oscillation and the square of the frequency of the incident light. This functional dependency is preserved when the helices are randomly oriented to the direction of the light, appropriate to the situation of molecules in the liquid or gas phase, explaining the rotatory dispersion discovered by Biot as corrected by Drude. These expressions are related to the rotation of a given amount of the substance comprising the molecules in question in the liquid or gas phase, and to the dimensions of the helices.

Kauzmann opens his discussion of the quantum mechanical account with the observation that the classical model “could explain the variation of the optical activity with the wave length [frequency] of the light used in the measurement” (1957, p. 704). This use of “explain” is comparable to that in the passage of Campbell’s in section 4 insofar as Kauzmann goes on to say that “one would hardly take this model seriously as a basis for a detailed theory of the relationship between molecular structure and optical rotatory power” (*loc. cit.*), although the deduction is, unlike anything in 19th-century atomism, hardly trivial and unedifying. The quantum mechanical treatment yields an expression determining the difference in the contribution of an absorption band of a given substance called the rotatory strength. Since the Hamiltonian commutes with the reflection operator, a molecule and its mirror image must have the same energy. Absorption therefore occurs at the same wave length, and any difference in optical rotation between two molecules, the one the mirror image of the other, derives entirely from the rotatory strengths, which are shown to be equal in magnitude but opposite in sign. This is the underlying explanation of the difference in rotation by optical isomers. Absence of rotatory power arises either because one of the induced electrical or magnetic dipole moments is zero, or because they are perpendicular, and divergence from these situations might be expected to form the basis of a more detailed account of the experimental details (1957, pp. 716–7). In his concluding discussion, Kauzmann says that the main interest in calculating optical rotations of asymmetric molecules is the “determination of the spatial arrangement of the groups in these molecules” (1957, p. 722). Unfortunately, no calculations to date, he goes on to regret, “can be said to be very reliable” (*loc. cit.*). Certainly on the classical theory of optics, sufficient detail must be ascribed to the sub-molecular structure that electrons can be identified moving in such a way as to give rise to appropriate changes in the electric and magnetic dipole moments. But he notes in particular that “[t]he reason for the lack of confidence in the

absolute configurations derived from classical theories of optical rotatory power is the incorrect detailed picture of the electronic motions on which the classical theories are based” (loc. cit.).

Even the link to the beginning of the century seems to be becoming more tenuous. In fact Kauzmann compares his “classical” model of rotatory power not to anything in Lorentz’s *Theory of Electrons*, but to a 1933 theory of Werner Kuhn’s. Lowry (1935, Chs. 28–30) provides a review of work in this period, noting that as late as 1916 Gray was lamenting the fact that the theories of chemists and physicists “have not been tied together; it has not been shown why the asymmetric molecule should give rise to [optical rotation]” (Lowry 1935, p. 358). In order to put Kauzmann’s derogatory remarks about what the classical theory of rotation says about the spatial structure of molecules into perspective and relate it to budding ideas on valency, a few words might be said concerning the extreme uncertainty about how electrons are incorporated into atomic and molecular structure during the period in question.

## 6. Uncertainty in the First Decades of the 20th Century

Views may differ on when the first proposals for atomic structure with any lasting import were made—the more stringent the requirement of overall coherence, the later the date. But even the most exacting views will surely allow that the Bohr atom of 1913 was a major source of inspiration of later theories even if its viability was subject to internal problems which were well known at the time. What seems to have made Bohr’s theory of interest, despite its incoherence as a stable structure, was the hope it held out for an understanding of spectra. During the previous decades, characteristic spectral lines had added to the stock of properties which could be used to distinguish elements and led to the discovery of a number of new elements which traditional chemical procedures had not revealed. Bohr’s was the first proposal with any claim to explain spectra,<sup>13</sup> and arguably provides a “core causal description” of the kind Psillos needs for his continuity thesis. Essentially the same idea, it could be argued, is retained in the wave mechanical explanation of atomic spectra, which also provides some account of the stability of atoms which eluded the young Bohr. It is hard to see that there were any antecedents prior to 1913. Much the same has been said of the theory of valency: “The first satisfactory picture of the chemical bond was proposed early in 1916 by G. N. Lewis” (Kohler 1971, p. 344).

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<sup>13</sup> It should be borne in mind, however, that for all elements except the hydrogen atom, Bohr’s theory read off electronic structure from the periodic table rather than deriving its features from general principles (see Scerri 1993).

To get some idea of the gulf between these and earlier theories, consider the conception of atoms in Jones (1902) mentioned in the Introduction. After the initial praise of Dalton, it transpires that Jones is not satisfied with indicating how the laws of constant and multiple proportions follow from Dalton's hypothesis, and he adds a section entitled "the nature of the atom." Here he sets great store by the conception of vortex atoms that Kelvin based on Helmholtz's demonstration of the preservation of vortex motion once created in a perfect fluid. But his reasons for thinking that J. J. Thomson's application of the theory to chemical phenomena, which he goes on to describe, counts any less as speculation than pre-Daltonian atomic theories of matter seem remarkably weak. Atoms may be simple rings or several linked together on this view. Jones is content to say that differences in volume of the simple rings "account for the difference in properties observed" (1902, p. 38) without indicating how. Chemical reaction occurs by union of vortex rings. When rings "of the same kind"—same volume?—unite, we have molecules of elementary substances; if different in kind, compounds. A united pair of rings brought into the presence of other vortex rings will separate since their translational velocities become different as the result of a differential change in their radii.

This, in Jones' view, was the stuff of explanatory mechanisms underlying the formation and constitution of chemical substances. An important prediction of the theory, he thought, was that it set an upper limit of six on the number of atoms that can be combined with another, corresponding nicely with the fact that a compound with compositional formula  $WCl_6$  is known, but no compound involving a compositional ratio greater than 1 : 6 was known. And despite "the enormous difficulties involved," Jones maintained that it "is by far the best theory that we have as to the nature of the atom" (1902, p. 39).

There is no hint of the electrons which are essential to Bohr's mechanism of spectral absorption and emission lines, and which were to play a central role in the debate on the character of valency immediately prior to the development of wave mechanical theories of the chemical bond in the late 1920s and early 1930s. The nub of this debate was the Lewis-Langmuir theory, which arose out of G. N. Lewis's 1916 paper on bonding. This development was by no means universally welcomed by chemists (Kohler 1975, pp. 443f. and *passim*). But the rise of physical organic chemistry in Britain in the 1920s was not, as the Kuhnian paradigm would have it, a revolution instigated by young men in response to a crisis (Kohler 1975, p. 467). It is rather the story of how middle-aged men, already interested in ideas of atomic structure and reaction mechanisms, perceived how older approaches could be adopted to the new perspective with the result that "[w]hat organic chemists did in their laboratories changed little after 1923" (Kohler 1975, p. 467). Perhaps this suggests some kind of

continuity with late 19th-century chemistry. But while critics deprecated their efforts as “metaphysics,” what these enthusiasts offered as replacement for Lewis’s initial cubic atom was a legion of ideas with a striking lack of agreement on details. In fact, Robinson—a leading light in the British school—“became uneasy about concrete atom models” and went so far as to describe Lewis’s octet rule as “more or less symbolic” (Kohler 1975, p. 465). The development of an interest in organic reaction mechanisms may have gone hand in hand with an interest in Thomson’s, Rutherford’s and Bohr’s ideas on atomic structure, and created a favourable environment for the reception of wave mechanical accounts of valency by highlighting the idea of a shared pair of electrons underlying the chemical bond. But it is difficult to see in these pre-Lewis-Langmuir roots more than the hope of finding any definite reaction mechanisms. There are no actual remnants of a mechanism from 19th-century chemistry, however rudimentary, underlying ideas of chemical reactions and the chemical structure of substances in the second and third decades of the new century, which could form the basis of a continuity of reference to atoms along the lines Psillos envisages.

Stark developed a theory of valency in 1908 which he subsequently applied to the problem of optical activity in 1914. Lowry describes this as the first attempt to give a chemist’s picture of the problem “in which optical rotatory power is produced not by a spiral vibrator, but by the association of four dissimilar radicals with an asymmetric carbon atom. Stark’s mechanism ... is not [however] found in modern theories ... [Nor does] the influence of one moving electron on the motion of others, which forms the basis of these theories,<sup>14</sup> ... play any part in Stark’s mechanism” (1935, p. 374). Mention might also be made of Allen’s 1920 theory of optical rotation (Lowry 1935, pp. 375–6) based on Parson’s magneton theory of atomic structure which Kohler (1971, pp. 364–70) suggests might have influenced Lewis. The quarter of a century interval separating the tetrahedral hypothesis from the rudimentary explanatory mechanism was an underestimate.

## 7. Concluding Remarks

The turning point for the atomic theory came with Einstein’s and Perrin’s investigations of Brownian motion around 1905. What the sceptics were forced to accept, despite quite good arguments for the incoherence of atoms, was the determination of Avogadro’s number. This determination, soon confirmed by independent methods, cast Loschmidt’s and Kelvin’s earlier estimates of atomic size and number in a better light. It might also be said that it provided a connecting link of the kind mentioned at the end of section 4 and strengthened evidence provided by the unusually long reaction times of

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<sup>14</sup> [cf. the opposed electrons in Kauzmann’s classical model]

certain organic reactions, for example the esterification of aromatic acids with large groups substituted in the ortho-position. Such considerations led Victor Meyer to propose his theory of steric hindrance in the mid 1890s, showing how the postulated shapes actually affect chemical processes and supporting a literal spatial interpretation of the tetrahedral structures which were proving so useful to organic chemists in the late 19th century. The British physical organic chemists described above built on kinetic studies of this kind. But this was ball and stick stuff. In providing evidence for the existence of atoms, it didn't really show how the incoherence arguments were to be met, as is well illustrated by the case of Bohr's theory. Although the existence of atoms could no longer reasonably be questioned, many problems remained unsolved, including those with which chemists were preoccupied concerning the nature of valency. A general assumption of the unity of science naturally suggested that there would be an atomic aspect of chemical phenomena to be described. Perhaps this general claim is sufficient to yield a continuity of sorts—the sort of continuity of tradition reaching back to Democritus which is more bland and correspondingly more difficult to deny. But this is a far cry from the claim that continuity of chemical theory is the result of an inference to the best explanation of chemical phenomena identifying rudimentary explanatory mechanisms whose core features have survived intact from Dalton's time.

Jones questioned this mundane tradition of atomistic thought when he denied continuity of reference with his radical division between the “scientific atomic theory” and older ideas. But although it followed the introduction of quantitative methods in chemistry, explanatory adequacy was not one of the distinguishing features of this schism. Dalton simply repeated the difference of chemical substances in a difference in weight of atoms, which hardly explains the differences among the elementary substances, for example their varying reactivities with other elements and abilities to combine in varying proportions. Nor does it provide a general, effective theoretical criterion for determining sameness of substance, as macroscopic thermodynamics was able to do (van Brakel 2000, pp. 84–7; Needham 2000, 2002a). Boyle, on the other hand, did at least envisage a structural explanation of sameness and difference of kind on the basis of sameness and difference of arrangements of his elementary corpuscles even if it was purely speculative (Chalmers 1993). Modern theory follows Boyle in attempting to understand the periodic table on the basis of different structures of elementary particles constituting the ultimate units of particular substances. As in Boyle's vision, it inevitably allows in principle for the transmutation of the elements, now known to be a real possibility. Ambition rather than achievement is perhaps a better mark of continuity.

That there is a more intimate basis of continuity, in terms of the preservation of explanatory mechanisms already discernible in 19th-century chemistry and corresponding to what Psillos calls a core causal description, is a much stronger and more controversial thesis. It requires a more definite articulation of the putative common explanatory threads than the vaguer notions of likeness that suffice for the weaker and more sweeping continuity claims just mentioned. Criticisms developed here suggest that there were no atomic mechanisms to be preserved from the 19th century explaining the idea of combination highlighted by the law of constant proportions, and even the situation with optical isomerism, though more subtle, is much the same.<sup>15</sup> Although the status of 19th-century atomism calls for a far more extensive investigation, the two themes considered here are central to the issue and give some indication of what the general position would be. The discussion gives some conception of what 20th-century chemistry has succeeded in explaining by drawing attention to the woefully inadequate explanatory power of classical atomism. 19th-century opponents of atomism were aware of these inadequacies, and their insights are gravely distorted by representing them as expressions of positivistic fixation on observation rather than criticism which helped to shape modern theory.

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<sup>15</sup> Nothing said here implies that it wasn't reasonable to work on atomic theories in the hope that they would illuminate problems of chemical combination while remaining agnostic on ontological commitment.

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