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# ATOMISM IN LATE NINETEENTH-CENTURY PHYSICAL CHEMISTRY

### By George M. Fleck

> There are . . . two modes of thinking about the constitution of bodies, which have had their adherents both in ancient and modern times. They correspond to the two methods of regarding quantity—the arithmetical and the geometrical. To the atomist the true method of estimating the quantity of matter in a body is to count the atoms in it. The void spaces between the atoms count for nothing. To those who identify matter with extension, the volume of space occupied by a body is the only measure of the quantity of matter in it.[1]

The extremely rapid elucidation of the microscopic structure of matter during the past half century has given chemists an assurance of the reality of the chemical atom and a faith that he who builds on the postulates of atomic theory is building on sure and solid foundations. It is important to realize that such assurance is not based on the findings of classical chemistry, and that indeed the best minds in physical chemistry at the close of the XIXth century were attempting to find a surer base for physical chemistry than chemical atomism, a concept which then had little direct experimental validation, and which did not appear to be particularly fruitful in predicting physical-chemical phenomena.

In spite of what would seem to be assumed about the existence of atoms by chemists who wrote structural formulae, Sir Oliver Lodge could say in retrospect in 1912:

> Although the atomic theory of chemistry has held its own, and although chemists have tried to picture to themselves the kind of atomic arrangement or grouping which would account for the observed properties of molecules —among other things for their crystalline interlockings and angular facets —yet chemists have always been careful to say that these pictorial representations were not to be taken literally or supposed to correspond with actual fact, but that they were to be treated in a more or less metaphorical or allegorical manner rather than as statements of reality. Indeed, the tendency was to doubt whether the actual *fact* of such arrangements could ever be perceived; and a good deal of scepticism persisted in the minds of at least a few chemists as to whether 'atoms of matter' were more than a convenient verbal expression.[2]

The modern chemical atom may be said to date from its formulation by John Dalton during the period from 1800 to 1803. The Daltonian atom was the subject of heated and confused argument for

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[1] James Clerk Maxwell, "Atom," *Encyclopaedia Britannica* (9th ed., Edinburgh, 1875), III, 36.

[2] Lodge, "Becquerel Memorial Lecture," *J. Chem. Soc.*, CI (1912), 2005.

a quarter century, fell into disrepute for another quarter century, and was revived quite convincingly in 1858 by Stanislao Cannizzaro in his *Sunto di un Corso di Filosofia Chimica.* This pamphlet, together with the work of Friedrich Kekulé in postulating the carbon-carbon bond (1858) and in using graphic formulae (1861), marked the beginnings of a rapid development of structural organic chemistry which in turn made possible correlation of a vast body of experimental data. Structural organic chemistry explicitly requires discrete atoms with fixed mass, fixed spatial orientation of chemical bonds stable in time, and distinct chemical identity. This is rigid Daltonian atomism applied to carbon chemistry, accepted then because it was a very good way to represent data and retained in large part today because it still is a very good way to represent data.[3]

With the contemporaneous rise of physical chemistry, serious questioning of the usefulness of the hypothesis of atomicity began again, led by and supported by important men in theoretical chemistry including Lord Kelvin (1824–1907), Wilhelm Ostwald (1853–1932), Josiah Willard Gibbs (1839–1903), Pierre Duhem (1861–1916), and Marcelin Berthelot (1827–1907). Alternate theories were proposed, a complete treatise on inorganic and physical chemistry was written without the assumption of atoms, and the formalisms of thermodynamics and of classical statistical mechanics were erected with an explicitly-stated independence of the nature of matter.

Why did these physical chemists find the atomic hypothesis of little use? The atomic theory throughout the XIXth century was an *ad hoc* theory which suffered from the fact that atoms as described by XIXth-century theorists were incapable of accounting for a host of physical phenomena which were being discovered. Organic chemists had called for a cease-fire on the questioning of valency and the mechanisms of chemical bonding, but no satisfactory answers had been given. Expediency decreed that organic chemists were to draw pictorial formulae and be temporarily satisfied with atoms, but physical chemists had less of a vested interest in atoms and asked, for instance, how polyatomic molecules of elements could be formed. What distinguished oxygen from hydrogen? How does an atom radiate energy to give the characteristic spectral lines? Why doesn't an atom chip into smaller pieces?

The first attempts to answer such questions about the atom were aimed at devising models of atoms which would have all the properties needed to give the observed macroscopic behavior of matter. William Rankine (1820–72) proposed an hypothesis of molecular vortices, remarkably close to the present-day theory, in 1849. His

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[3] A good treatment of Dalton's atomism is Leonard K. Nash, "The Atomic-Molecular Theory," Case 4 of *Harvard Case Histories in Experimental Science* (Cambridge, Mass., 1957).

molecular vortices had nuclei with particulate elastic atmospheres revolving about the central nuclei. Discussing this theory in 1855, he stated his philosophy of experimental investigation:

> the laws of the expansive action of heat are deduced from a mechanical hypothesis, called that of Molecular Vortices. Those laws are capable of being expressed and proved independently of any hypothesis; but it is nevertheless considered that a molecular hypothesis, which has already led to the anticipation of some laws subsequently confirmed by experiment, may possibly lead hereafter to the anticipation of more such laws, and may at all events be regarded as interesting in a mathematical point of view; although its objective reality, like that of other molecular hypotheses, be incapable of absolute proof.[4]

Rankine used his molecular vortex theory to derive equations of elasticity and thermodynamics. Nevertheless, the Rankine model had certain serious flaws. Rankine postulated the elastic outer layer, but gave no reason why it should exist and why it should be elastic. He gave no answer to the question of why the elastic atmosphere should remain associated with the nucleus.

In 1867 Sir William Thomson (later Lord Kelvin) proposed that the "true atom" was a vortex in a perfect liquid, the perfect liquid presumably being the ether. With this theory he was able to preserve a discreteness in matter while at the same time maintaining an ultimate continuity, since the vortices were discrete whirlpools within the ether continuum. He based his theory on a paper[5] by Hermann Helmholtz (1821–94) in which Helmholtz derived expressions which show that in a frictionless, isotropic fluid of uniform density, vortices once formed would continue to undergo characteristic unceasing vortex motion and would retain their identity forever. Thomson opened his paper in the following manner:

> After noticing Helmholtz's admirable discovery of the law of vortex motion in a perfect liquid—that is, in a fluid perfectly destitute of viscosity (or fluid friction)—the author said that this discovery inevitably suggests the idea that Helmholtz's rings are the only true atoms. For the only pretext seeming to justify the monstrous assumption of infinitely strong and infinitely rigid pieces of matter, the existence of which is asserted as a probable hypothesis by some of the greatest modern chemists in their rashly-worded introductory statements, is that urged by Lucretius and adopted by Newton—that it seems necessary to account for the unalterable qualities of different kinds of matter. But Helmholtz has proved an absolutely unalterable quality in the motion of any portion of a perfect liquid in which

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[4] William John Macquorn Rankine, "On the Hypothesis of Molecular Vortices, or Centrifugal Theory of Elasticity, and its Connexion with the Theory of Heat," *Phil. Mag.*, ser. 4, X (1855), 411.

[5] H. Helmholtz, "On Integrals of the Hydrodynamical Equations, which express Vortex-motion," *Phil. Mag.*, ser. 4, XXXIII suppl. (1867), 485; "from Crelle's *Journal*, LV (1858), kindly communicated by Professor Tait."

the peculiar motion which he calls "Wirbelbewegung" has been once created. Thus any portion of a perfect liquid which has "Wirbelbewegung" has one recommendation of Lucretius's atoms—infinitely perennial specific quality.[6]

In addition, other desirable properties are possessed by these vortices. All their properties are derived by mathematical processes from the two assumptions of perfect ether and an initial creative act of setting the vortices in motion, whereas previous atomic theories had assigned properties to the atoms with a rather arbitrary abandon, assuming first, for instance, indivisible atoms, and then giving them the *ad hoc* characteristics of hardness, impenetrability, and quite specific forces of repulsion and attraction. Thomson's vortex atom is automatically perfectly elastic, according to the equations which govern its motion, and Thomson felt that a rigorous kinetic theory could be derived from the vortex-motion equations. He was equally confident that the thermal expansion coefficient could be calculated from the swelling of the vortex with increasing kinetic energy, and that the spectral lines could be calculated from the modes of vibration associated with the vortex. The possibilities for thus explaining and correlating the rapidly increasing collection of spectral data from first principles was especially intriguing.

Thomson's theory led P. G. Tait to extend his investigations on the analytic geometry of knots, Tait feeling that a mathematical treatment of involved intertwining and knotting of vortices would be necessary for a complete vortex atom theory.[7]

Vortex atoms can be demonstrated in a dramatic manner by means of smoke rings which simulate the motion and interaction of ethereal vortices. It has been said that a lecture demonstration of smoke rings by Tait early in 1867 to illustrate Helmholtz vortex motion gave Thomson the idea of the vortex atom.[8] Tait described an apparatus suitable for producing smoke rings and the various ways in which the rings could be used to show properties of vortex atoms.[9] Shortly after the first publication by Thomson, the *Philosophical Magazine* carried a report [10] by Robert Ball who told of demonstrating vortex rings at an evening scientific meeting of the Royal Society of Dublin. Apparently everybody there had a chance to blow smoke rings and watch the curious effects produced by collisions of the rings.

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[6] Sir William Thomson, "On Vortex Atoms," *Phil. Mag.*, ser. 4, XXXIV (1867), 15.

[7] Peter Guthrie Tait, *Scientific Papers* (2 vols., Cambridge, 1898), I, 270–347; papers originally published 1876–1885.

[8] Cargill Gilston Knott, *Life and Scientific Work of Peter Guthrie Tait* (Cambridge, 1911), 68.

[9] P. G. Tait, *Lectures on Some Recent Advances in Physical Science* (London, 1876), 291.

[10] Robert Ball, "On Vortex-rings in Air," *Phil. Mag.*, ser. 4, XXXVI (1868), 12.

Thomson's vortex theory received a warm reception in scientific circles, although it is difficult to judge whether this was because of the inherent scientific value of the theory or rather because of the dramatic appeal of smoke rings and the respect given to Thomson himself. The position of leadership held by Thomson was significant, and the spreading of the gospel gained impetus when Thomson was made a member of the three-man board of editors of the *Philosophical Magazine* in 1871. Thereafter a constant stream of articles appeared in the journal questioning the classical atomic theory.

One of the several authors of articles appearing during this period on the atomism controversy was Edmund Mills, and a representative passage gives some of the arguments being used against chemical atomism:

> In the antagonism between continuity in mathematics and alleged absolute limits in chemistry, we see the reason why so few chemists are mathematicians, and so few mathematicians chemists. . . . Chemistry still looks with half-averted face upon all dynamical doctrines. But her great centres of historic conflict are intelligible only by their aid. Acid, Alkali, Base, and Salt are not capable of definition as particular things; the principle of continuity alone renders them clear. Chemical Substance is homogeneous, not discontinuous substance; Chemical Functions are modes of motion. The Atomic Theory, triumphant still, is more suspected than before; but it is indeed a better servant to pure dynamics; for it places before the mind, daily and most distinctly, the fatal consequences of the assumption that quantity consists of parts. Grave and mature chemists now investigate the position of a particular atom in an aromatic compound, and find it at the side, in the middle, or near some other portion of an open or closed chain. In the mean time we hear nothing of the chemical process.[11]

Mills noted several significant trends in chemistry. He pointed out that the mathematics of continuous functions is not adequate to deal fully with particulate matter. This fact was to be an important factor in causing mathematical physical chemists to disregard the possible atomic structure of matter in formulating their theories; the mathematics is much more elegant if one assumes continuous matter. Secondly, the principle of continuity was one which was becoming fashionable and one which was to be expanded by Ostwald in his revolt against atomism. Thirdly, it is interesting to note that organic chemistry was having trouble with its structural formulae when various rearrangements were encountered, and embarrassing bits of information from organic laboratories were being used in opposition to the organic chemist's atomism.

James Clerk Maxwell seems to have accepted the vortex atom as a possible representation of reality, and remarked that

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[11] Edmund J. Mills, "On Statical and Dynamical Ideas in Chemistry.–Part IV. On the Idea of Motion," *Phil. Mag.*, ser. 4, XLVI (1873), 398.

> the vortex ring of Helmholtz, imagined as the true form of the atom by Thomson, satisfies more of the conditions than any atom hitherto imagined. . . . But the greatest recommendation of this theory, from a philosophical point of view, is that its success in explaining phenomena does not depend on the ingenuity with which its contrivers 'save appearances' by introducing first one hypothetical force and then another (*loc. cit.*).

Thomson did one thing with his atoms which today's physicists can't do; he explained gravitation. Vortices coming from outer space would collide with objects near the earth, but there would be no counterbalancing force, since the earth would stop most vortices coming from the opposite direction. The resultant force would be directed toward the earth and would appear to the terrestrial observer as the force of attraction called gravity (*ibid.*). This was a revival of LeSage's ultramundane corpuscle theory of gravitation of 1818.

Nevertheless, the vortex atom was essentially a compromise and failed to be satisfactory for all purposes. It had been devised in an attempt to retain ultimate continuity of matter by starting with the ethereal plenum, but the perfect ether continuum soon had a very definite particulate quality. The vortices had to be treated individually. It is difficult to retain for long a physical continuum, even though a continuum has an esthetic beauty of perfection which is enticing. Continuity has been assumed for such entities as the ether, the luminiferous ether, and the electric ether, but in each case workers in the fields have had to introduce an atomicity. Maxwell could say that there was an ether, but he wasn't sure whether it was continuous or atomistic.[12]

Not withstanding the speculations on the ultimate nature of matter, no satisfactory picture was being formulated. It was in such a situation that theoretical chemists found themselves in the last third of the century, and the response by several of the major contributors and leaders in the field of physical chemistry was to ignore speculations about atomicity and to organize physical chemistry about more easily demonstrable assumptions about the physical world. Such an attitude was stated by C. R. A. Wright:

> the main salient facts and generalizations on which chemical philosophy is founded are capable of expression in words, and of representation by the symbols in ordinary use, without in any way involving the ideas bound up in the hypothesis of the existence of material atoms as devised by Dalton (in its chemical relations) and subsequently extended; and secondly, that this hypothesis, though affording a clear *raison d'être* for many of these facts, is yet incapable of accounting readily for all of them—in other words, that the conceptions involved in this hypothesis are both unnecessary and insufficient.[13]

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[12] J. C. Maxwell, "Ether," *Encyclopaedia Britannica, ed. cit.*, VIII, 568.

[13] C. R. A. Wright, "On the Relations between the Atomic Hypothesis and the

Wilhelm Ostwald was one of the leaders in the move to organize physical chemistry on other bases than atomism. Ostwald, as founder (1889) and editor of the *Klassiker der exakten Wissenschaften* and as founder (1887) and co-editor of the *Zeitschrift für physikalische Chemie,* was a leader in scientific thought and his writings had substantial influence. He wrote a complete text of inorganic and physical chemistry in 1900 in which he explicitly rejected hypotheses concerning an atomic or molecular nature of matter. It was considered important enough to be translated from the German for an English edition. A selection dealing with definition of molar weight is illustrative of his position:

> The ratio of the weight of a given gas to that of an equal volume of the normal gas under the same conditions, is called its molecular weight or its molar weight. Since the former name has been derived from certain hypothetical notions regarding the constitution of the gases, notions which are not essential to the actual facts, we shall give preference to the name molar weight, although at present, the other is still the one most used.[14]

As Faraday Lecturer to the Chemical Society of London in 1904, Ostwald presented derivations which showed that

> It is possible, to deduce from the principles of chemical dynamics all the stoichiometrical laws; the law of constant proportions, the law of multiple proportions and the law of combining weights. . . . Chemical dynamics has, therefore, made the atomic hypothesis unnecessary for this purpose and has put the theory of stoichiometrical laws on more secure ground than that furnished by a mere hypothesis.[15]

Pierre Duhem, one of the outstanding contributors to thermodynamic theory, had as a major goal in life the formulation of thermodynamic principles in such a way as to free the discipline from models and mechanistic explanations. He had little respect for atomism. In 1906 Duhem presented a detailed positivistic analysis of physical theory in which he rejected atomistic explanations of matter and challenged the utility of atomic theories in the development of physics and physical chemistry. Prefacing the second edition of this book in 1914, he reaffirmed his principles stated eight years before.[16]

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Condensed Symbolic Expressions of Chemical Facts and Changes known as Dissected (Structural) Formulae," *Phil. Mag.*, ser. 4, XLV (1872), 241.

[14] W. Ostwald, *The Principles of Inorganic Chemistry* ("translated with the author's sanction by Alexander Findlay," London, 1902), 89. Translation of *Grundlinien der anorganischen Chemie* (1900).

[15] W. Ostwald, "Elements and Compounds," *J. Chem. Soc.* (1904), 506.

[16] P. Duhem, *La Théorie physique* (Paris, 1906$^1$, 1914$^2$); English translation: *The Aim and Structure of Physical Theory,* trans. by Philip P. Wiener (Princeton, 1954).

Josiah Willard Gibbs, in perfecting chemical thermodynamics and in establishing statistical mechanics, based his work on hypotheses which he believed to be specifically independent of the intimate structure of substances. In developing his thermodynamics, he points out that "the choice of the substances which we are to regard as the components of the mass considered, may be determined entirely by convenience, and independently of any theory in regard to the internal constitution of the mass."[17] In the introduction of his *Statistical Mechanics* he states:

> Moreover, we avoid the gravest difficulties when, giving up the attempt to frame hypotheses concerning the constitution of material bodies, we pursue statistical inquiries as a branch of rational mechanics. In the present state of science, it seems hardly possible to frame a dynamic theory of molecular action which shall embrace the phenomena of thermodynamics, of radiation, and of the electrical manifestations which accompany the union of atoms. . . . Certainly, one is building on an insecure foundation, who rests his work on hypotheses concerning the constitution of matter.[18]

As would have been expected, Ostwald highly approved of Gibbs' approach. Ostwald observes in his autobiography that "Gibbs deals almost exclusively with energy and its factors and holds himself free from all kinetic hypotheses. Because of this, his results possess a certainty and a lasting quality of the highest degree humanly attainable."[19]

Well aware that the work of Gibbs was ammunition for his non-atomism fight, Ostwald translated the papers on thermodynamics into German and did his best to promote the method of Gibbs in Europe.

Such was an important trend of thought in the late XIXth century, and there was reason to believe then that new progress in physical science would continue to move chemistry away from atomism in the XXth century just dawning. As late as 1907 Ostwald was still pursuing this course, attempting "to work out a chemistry in the form of a rational scientific system without bringing in the properties of individual substances."[20] Illustrative of the continuing influence

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[17] J. W. Gibbs, "On the Equilibrium of Heterogeneous Substances," *Transactions of the Connecticut Academy*, 3 (1876–1878); *The Collected Works of J. Willard Gibbs* (2 vols., New Haven, 1948), I, 63.

[18] Gibbs, *Elementary Principles in Statistical Mechanics developed with especial reference to the Rational Foundation of Thermodynamics* (New York, 1902); *Collected Works*, II, ix.

[19] Quoted in the form of a free translation by Lynde Phelps Wheeler, *Josiah Willard Gibbs* (New Haven, 1952), 99.

[20] Ostwald, *The Fundamental Principles of Chemistry* ("authorized translation by Harry W. Morse," London, 1909), vi; German ed., 1907.

which Ostwald had is a passage taken from an important American book on physical chemistry book published in 1918:

> While the atomic theory has played a very important part in the development of modern chemistry, and while we recognize that it helps to clarify our thinking and enables us to construct a mental image of tiny spheres uniting to form a chemical compound, yet we must not forget the fact that these atoms are purely hypothetical. . . . Ostwald believes that in the not distant future the atomic theory will be abandoned and chemists will free themselves from the yoke of this hypothesis, relying solely upon the results of experiment. He says: "It seems as if the adaptability of the atomic hypothesis is near exhaustion, and it is well to realize that, according to the lesson repeatedly taught by the history of science, such an end is sooner or later inevitable."[21]

However, Duhem in 1906 and Ostwald in 1907, protagonists of the non-atomism school, were not the prophets of a new order, but had become the last vestiges of an old order.[22] By 1907 physicists had begun to come to experimental terms with atoms. The investigations of J. J. Thomson with gaseous ions and electrons (1894 *et seq.*), Henri Becquerel with radioactivity (1896), Max Planck with his new quantum theory (1900), Albert Einstein with the photoelectric effect (1905) and Brownian motion (1905), and Jean Perrin with colloidal systems (1909) were providing the experimental and theoretical foundations for the nuclear atom of Niels Bohr (1913) which was to prove to be one of the most adaptable and fruitful unifying concepts in chemistry.

Physical chemistry, with immediate origins as a separate discipline in the late XIXth century, was brought into being by men who were sceptical of rigid chemical atomism, whose minds were open to improvements or changes in the concept of the atom, and who were willing to ignore the atomic theory if it seemed that greater generality could thereby be achieved. It is significant that one of the great physical-chemical theories of the XIXth century, the formalism of thermodynamics, owes its generality and usefulness precisely to its independence of the nature of the intimate structure of matter.

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[21] F. H. Getman, *Outlines of Theoretical Chemistry* (New York, 1918$^2$), 7–8.

[22] Bancroft [Wilder D. Bancroft, *J. Chem. Ed.*, X (1933), 539] points out that in an 1895 lecture Ostwald stated: "The previous infertility of the atomistic doctrine has been modified and many new facts have come to light as the years go by. This eliminates the hypothetical nature of the atomic theory and makes it a legitimate branch of experimental physics and chemistry." Ostwald was certainly aware of developments in physics, but he continued to believe that since man's knowledge of the properties of atoms was fragmentary and unsure, it was better for physical chemists to base their theories on more solid foundations.