

ISOBEL FALCONER*

A point in common? The electron in chemistry and physics 1890-1914

Summary – This paper gives a brief overview of the early history of the electron in chemistry – a period that has been generally neglected. I concentrate on experimental work, particularly that of J.J. Thomson. I suggest that the inability of chemists to experiment directly on the electron underlay the lack of a sense of ownership of the electron that has been identified by other authors. For a brief period the powerful reductionist promise of the physicists' dynamic electron held back chemists in their attempts to develop electron theories of bonding, but when the reductionist programme faltered, chemists were quick to develop their own agenda.

Keywords: electron history, electron in chemistry, atomic structure, valence, chemical bonding, J.J. Thomson

Introduction

The history of the electron in chemistry has been relatively neglected. When, nine years ago the centenary of the discovery of the electron sparked a plethora of historical publications, a crude estimate is that only a very small proportion – not more than 10% – were by historians of chemistry; the bulk concerned the physics and metaphysical status of the electron. This might seem surprising when a naïve view of the two disciplines suggests that these days the electron is more fundamental to chemistry, mediating the interactions between substances, than it is to physics where it is now one of a multitude of elementary particles and unity is sought at a deeper level. Two historians though do touch on reasons for this relative neglect by chemists, and establish a context for this paper.

Mary Jo Nye, following the pragmatic philosophy of many present-day

* Research Associate, Faculty of Arts, Open University, UK *Address:* Lumbo Farmhouse, St Andrews, Fife, UK, KY16 8NS; telephone +44 1334 478507; email ijf3@tutor.open.ac.uk

chemists, argues that while the electron provided a supporting rationale for the organising schemata of chemistry, it did not compel a change in these schemata, which had been arrived at by other, empirical, means; the subject matter of chemistry did not change, and hence the electron was not viewed as revolutionary by chemists. She describes the assimilation of the electron into organic chemistry up to the meeting on “The Electronic Theory of Valence” of the Faraday Society in Cambridge in 1923, which she takes as marking full recognition of the importance of the electron as a material particle which mediated the valence bond. But the bulk of her paper explores the later implications of this assimilation (Nye 2001). Kostas Gavroglu accepts a chronologically similar periodisation, but asserts that it had its origin in an explicit methodological difference between the two periods (Gavroglu 2001). He suggests that prior to 1926 physicists and chemists were united in a common enquiry, viewing the electron as a benevolent explanatory entity in both disciplines. However, following the success of the Schrödinger equation in the one electron case, and the advent of the relativistic and spinning electron, physics was reinstated as the paradigmatic science and claimed the electron for its own, while chemists, realising that the multi-electron case was too intractable for practical purposes, pursued a deliberately divergent, semi-empirical methodology which accords with that described by Nye. Like Nye, though, Gavroglu concentrates on the later period, and does not explore the earlier commonality, what it consisted of, or how it was arrived at. An earlier, related paper (Arabatzi and Gavroglu 1997), partially fills this gap, identifying a chasm that opened up around 1915 between a physicist’s non-magnetic electron which obeyed Coulomb’s law, and the chemists’ magnetic electron which violated Coulomb’s law at small distances. This difference, he suggests, was the origin of the differing approaches of chemists and physicists to the ‘atom’ as an explanatory entity (Gavroglu 1997). In the case of the atom, he argues that a similar period of commonality had focused around the vortex atom. The vortex atom was a ‘physicists atom’ consisting of vortex rings in the ether, which had been developed by William Thomson, J.J. Thomson and others, and offered an explanation of valence and molecular bonding. Gavroglu suggests that those chemists, predominantly British, who adopted atoms as an explanatory principle – and there were many of the Continental ‘Energeticist’ school who did not – had gone too far in their enthusiasm for the physicists’ entity and, from the 1890s on, struggled to re-assert the billiard ball ‘chemists’ conception of the atom. However, in these papers, Gavroglu’s approach is ontological, and he argues that the main theme of the history of the electron in chemistry should be concerned with the role of the electron in theory building; the corollary is that other aspects of the relationship between electrons, chemistry and physics, are neglected (Gavroglu 2001).

In this paper I make a start at addressing these two gaps – lack of examination of the basis of commonality, and other aspects of electron history – by taking a look at some of the experimental practice surrounding electron research up to around

1914, and in doing so cast further light on the contention that chemists did not feel that they ‘owned’ electrons in the way physicists did.

Characterising the electron

The term ‘electron’ itself was first used by George Johnstone Stoney in 1891, and he coined it in the course of work that was specifically designed to resolve problems at the interface of physics and chemistry – an investigation into the origins of spectra (Stoney 1891; O’Hara 1993).

Since the discovery of characteristic spectra in 1860, spectrum analysis had become a rich and productive tool for chemists in identifying elements and, in particular, in discovering new ones. This richness was not without its problems though, and the increasing diversity of elements helped to prompt renewed attempts to find underlying organising principles, some of which, such as Crookes’ and Lockyer’s evolutionary theories were essentially based on Prout’s hypothesis of a universal building block for atoms (Lockyer 1881; Crookes 1886; Kragh 1982; Leone and Robotti 2000). If we characterise these attempts in Gavroglu’s terms, Crookes’ and Lockyer’s atoms represent an intermediate position between the Daltonian billiard ball ‘chemists atom’ and the ethereal, dynamical ‘physicists atom’.

The real problems arose, though, when spectral phenomena were moved into the context of physics, and the solutions suggested represent the physicists’ approach. Physicists had become interested in the structure of atoms following the success of the kinetic theory of gases which proposed that large scale effects such as heat could be explained by the motion of atoms and molecules (Clausius 1857; Maxwell 1860). Some idea of atomic structure was needed to find out what sorts of vibration might be present. However, models devised to satisfy kinetic theory, based on chemical atoms and molecules, failed to account for the complexity of spectral phenomena or the dispersion of light (O’Hara 1993; Carazza and Robotti 1996). Electrodynamical models of the atom were suggested by Lorentz, Kolacek, and Ebert as a possible solution, but ran into the further difficulty of reconciling the discrete nature of electric charge implied by Faraday’s laws of electrolysis with the continuum required by Maxwell’s electromagnetic theory – a theory that had just received apparent experimental justification in Hertz’s demonstration of radio waves (Lorentz 1878; Hertz 1886; Kolacek 1887; Ebert 1893).

In 1874 Stoney was probably the first to suggest that Faraday’s laws implied that electricity was “quantised” and that the same quantity of electricity was associated with each chemical bond and Helmholtz made a similar suggestion in 1881 (Stoney 1874; Stoney 1881; O’Hara 1993). Now, in 1891, Stoney went further, suggesting that spectra were due to undulations in the luminiferous ether created by periodic vibrations of a unit of electric charge, which he called an electron, orbiting within the molecule. An electron was associated in the chemical atom with each bond (O’Hara 1993). Similar suggestions were made by Ebert, Richartz, and

Schuster (Richartz 1891; Ebert 1894; Schuster 1894-5). Stoney's work was taken up explicitly by Joseph Larmor, in his papers on 'A dynamical theory of the electric and luminiferous medium' (Larmor 1894; Larmor 1895; Larmor 1897). Larmor adopted the 'electron' terminology, following a suggestion by George FitzGerald, but, as the title shows, his interests were much more clearly physical than Stoney's, in establishing the relations between electricity, light and matter. In its dynamical and ethereal approach, Larmor's was very definitely a 'physicist's atom' in Gavroglu's terms, as was that of Henrik Lorentz whose electromagnetic theory of matter paralleled Larmor's.

I've given an extremely brief sketch of the context of atomic research by 1895. The most significant point to note is that this was a theoretical context – there *was* no direct experimental context – the theories were inferential and neither physicists nor chemists had any means of experimenting directly on the structure of atoms.

Over the next two years the situation was to change dramatically: in 1896 Pieter Zeeman demonstrated the magnetic splitting of spectral lines, which he interpreted in terms of Lorentz's electromagnetic theory; and in 1897 following up on the discovery of x-rays, Emil Wiechert, Walter Kaufmann and Joseph John Thomson all independently measured the charge to mass ratio of cathode rays, finding it to be about 1000 times larger than that of the H⁺ ion (Zeeman 1896; Kaufmann 1897; Thomson 1897a; Thomson 1897b; Wiechert 1897). These experiments are conventionally taken as representing the 'discovery of the electron'. Of the four, Thomson was the only physicist with sufficient interest in chemistry to view his measurements within a chemical context as well as a physical. He came from the British tradition, described by Gavroglu, where chemists were, for the time being, working much more closely alongside physicists than they were on the Continent. He was an associate of Larmor's and had been experimenting on molecular dissociation in gaseous discharge since developing his vortex atom theory in 1882 (Thomson 1883; Falconer 1987; Chayut 1991). Thomson went way beyond the limitations of his experimental data, when he suggested that the cathode ray particles were very small sub-atomic charged particles that might be the universal building blocks of atoms and proposed an atomic model based on them, which included an account of molecular bonding.

Thomson called his atomic constituents 'corpuscles', and the only precedents that he cited for his theory were Prout's and Lockyer's theories of divisible atoms – chemical, rather than physical, precedents (Thomson 1897). Chayut has elucidated Thomson's commitment to chemistry, and I have described elsewhere the conceptual development that led him to this interpretation of his cathode ray results (Falconer 1987; Chayut 1991). It seems that, however much Thomson may, or may not, have been influenced in this development by a 'physicists atom', he was now deliberately divorcing his atomic theory from that of the physicists, and trying to move closer to the chemists.

Apparently, this attempt failed, for the significance of Thomson's work in pro-

viding experimental evidence for a physicists' electron was realised instantly by FitzGerald, and his results were very rapidly moved, by physicists, into the evidential context of the Larmor and Lorentz theories, and his corpuscles became known as electrons (Falconer 1987; Falconer 2001).¹ I would like to suggest that one of the reasons why this happened – or rather, why chemists allowed this to happen – was that the experimental practices Thomson employed were those of a physicist. In his cathode ray work, although he moved theoretically towards the chemists, at the same time his experiments moved towards those of the physicists.

Gaseous discharge is the phenomenon seen when a glass vessel (the discharge tube) is filled with gas at low pressure and an electric potential is applied across it. The effects usually take the form of a glow in the tube, or fluorescence of the glass. They depend considerably on the pressure of gas in the tube, its chemical nature, the shape of the tube and electrodes, and the electric potential applied. Experiments typically involved varying and measuring these parameters and observing the appearance of the resultant glow. The results were communicated in the literature by sketches or engravings of the glow (Falconer 1985), and in the sense that they were characterised by their visual appearance, the practice of discharge research bore some resemblance to that of chemical spectrum analysis. It fell far short of the rigorous quantitative standards of British physicists such as Maxwell, Rayleigh and Kelvin. Discharge research also relied on glassware, and glass blowing techniques, that were common skills among chemists, but very little known among physicists. Thomson who had been experimenting on gaseous discharge, in the Cavendish Laboratory at Cambridge, since 1884, frequently found his work held up for lack of a skilled glass blower until, in 1887 he poached an assistant from the neighbouring chemistry laboratory; he employed Ebenezer Everett as a personal assistant for the next 40 years (Rayleigh 1942).

A very small group of physicists, Thomson included, had sought more quantitative and physical ways of characterising gaseous discharge. Hertz, for example, in 1883, had investigated the relation between the visible discharge and the current passing through the tube, and Schuster, in 1890, had tried to measure the speed of the discharge (Hertz 1883; Schuster 1890). But by and large these attempts were unsuccessful, and Thomson's *Recent Researches in Electricity and Magnetism*, published in 1893, chronicles their failure (Thomson 1893). Although a mass of quantitative results had been accumulated, it was far from clear which were genuine effects and which were caused by chemical processes at the electrodes. There was little agreement about the results or their significance in the absence of any unifying theory, and Thomson still relied significantly on visual, qualitative, methods. For example, as late as 1895, in 'A method of comparing the conductivity of badly

¹ Thomson continued to call the cathode ray particles 'corpuscles' until around 1913. However, to avoid confusion, I refer to them as electrons throughout the rest of this paper, regardless of the author I am discussing.

conducting substances', he assessed the conductivity visually by the effect of the substance on the brightness of discharge, even here where he was aiming at a characterisation by the physicists' notion of conductivity (Thomson 1895). And from 1893-1895 the focus of his research was in trying to elucidate the impact of chemical processes on the discharge (Thomson 1894; Thomson 1895).

In 1896, though, following the discovery of x-rays, Thomson, along with many other physicists, turned his attention to the cathode rays that caused them. Cathode rays form a special subset of discharge phenomena, observed only at very low pressure. They were discovered by Julius Plucker in 1858, and were known to travel in straight lines from the cathode and cause fluorescence on the wall of the tube where they hit it (Plucker 1858). However, the only known way of altering the path or appearance of the rays was by deflecting them in a magnetic field; they were unaffected by changing the nature of the gas in the discharge tube or the electrodes. Perrin had shown that they carried an electric charge, and Thomson now showed that they could also be deflected by an electric field (Perrin 1895; Thomson 1897). The essential point here is that the methods that Thomson, and Wiechert and Kaufmann, used in their cathode ray work were those of the physicist – manipulating them with electric and magnetic fields, measuring the heat they generated on hitting a thermocouple, their velocity, and the magnitudes of their deflections. And his characterisation of the corpuscle in terms of its charge, mass and velocity, was emphatically physical, rooted in the nineteenth century physicist's commitment to matter in motion as an explanatory framework.

If we consider the contention that what makes an entity 'real' is our ability to manipulate it (Hacking 1983), then we can perhaps see why a discontinuity opened up in chemists' and physicists' approach to, and ownership of, electron research, at the very point of the electron's conventional discovery. For physicists, the electron was now 'real'. They had ways of producing it, 'twisting its tail', pushing, pulling and measuring it, and generally subjecting it to systematic investigation. And this is just what they did. Kaufmann, in particular, spent the next eight years investigating the constitution of the electron, its mass, charge distribution, size and shape under various circumstances.

Chemical methods, on the other hand, proved useless for manipulating corpuscles or electrons. But that this would be so was not immediately apparent at the outset. An editorial note in *The Electrician* (1897) on Thomson's corpuscle theory suggested that the difficulties were practical, rather than ontological: corpuscles could not be analysed chemically because it would take too long to accumulate enough of them. A few chemists, the French physical chemist Paul Villard for example, did try investigating the chemical properties of cathode rays, but they failed to characterise the rays in chemical terms. Although Villard was convinced of the particulate nature of cathode rays, his main concern was to identify the chemical substance of which they were composed: the difference between him and Thomson is an ontological one (Lelong 2001). For Thomson the question of the

substance of cathode rays was meaningless because ‘substance’ was defined at the level of chemical atoms, while for Villard, an energeticist, the size of the cathode ray particles was irrelevant because what defined a substance was its chemical properties. Thus his experiments focused on the chemical effects of the rays, bouncing them off metallic plates coated with materials of known composition, such as lead sulphate, to obtain characteristic reactions. When he found that platinum plates were darkened by the rays, conversely copper oxide plates became bright, he interpreted these as evidence of chemical reduction and concluded that the rays were hydrogen (Villard 1898). But he failed to demonstrate any further chemical characteristics of the rays, and abandoned his hydrogen conclusion in 1908, acknowledging that light could also cause reducing effects (Villard 1908).

Thus chemical methods of manipulation failed to produce any useful chemical characterisation, and throughout Villard, in common with other chemists experimenting on cathode rays, was reliant on physicists’ means of producing the rays in a discharge tube. For chemists, then, electrons did not acquire any manipulative reality; chemists did not develop any sense of ‘ownership’ of electron theory, and electrons remained an organising principle. As Nye has pointed out, other organising principles, based on chemical properties of substances, were both possible and practical.

Electrons as an explanatory principle

In both disciplines the experimental results acquired importance by being put into theoretical practice. In the case of physics, electron theory offered a tantalising promise of unification. A wide variety of hitherto unrelated experimental phenomena, from gaseous to metallic conduction, to dispersion and radioactivity, could be encompassed. And the suggestion that all matter might be electromagnetic in origin, first made by Larmor (1895), promised fundamental advances, and became the focus of both experimental and theoretical attention. The debate hinged critically on the assumptions made about the conformation of the electron, as discussed by (Hon 1995). For example, in 1901 Kaufmann attempted to discover experimentally whether the electron had purely electromagnetic inertia, aiming to measure the speed, as well as the charge to mass ratio, of beta rays (by now identified with electrons) as accurately as possible and hence determine the relation between actual and apparent mass (Kaufmann 1901). Kaufmann turned the inhomogeneity of the velocity spectrum of radioactive emissions to good effect, passing the rays emitted from a speck of radium bromide between parallel electric and magnetic deflection fields which spread the beam into a curve on a photographic plate at the end of the tube. The coordinates of points along the curve were measured to find the corresponding relationship between the velocity and charge to mass ratio. His results showed qualitatively that the charge to mass ratio of the particles decreased markedly as the speed of the particles increased, suggesting that a significant pro-

portion of the apparent mass was electromagnetic in origin. Quantitative analysis, though, required a formula for the field energy of a rapidly moving electron. Kaufmann initially used Searle's model of the electron as a spherical shell over which charge is uniformly spread, and obtained the result that only one-fourth to one-third of the mass was electromagnetic (Searle 1897). Dissatisfied with this result, Max Abraham critically examined Searle's model, and suggested instead that the electron be treated as a rigid sphere with charge distributed uniformly either on its surface or through its volume (Abraham 1902). Analysing Kaufmann's results on this basis he found the entire mass to be electromagnetic, a result that seemed physically preferable, and Kaufmann adopted Abraham's electron model (Kaufmann 1902). Thomson also took up Kaufmann's results, but he applied his own ideas, treating the particle as a mathematical point, in order to justify a purely electromagnetic theory of mass (Thomson 1904).

For physicists then, the electron was a potential explanation for the whole of matter; the question of what it was made of was irrelevant, as long as it had the required spatial and charge distribution properties. Experiments were used, not to establish the composition of the electron, but to establish the requirements. The experimental technologies used were those of a physicist – and a highly skilled physicist.

Although they lacked the means to manipulate electrons, some chemists, particularly in America where energeticist, anti-atomic, principles held less sway, were also quick to take up the electron as an explanatory principle (Stranges 1982). Like the physicists, their concerns were not with the composition of the electron, but with its effects: could these explain the periodic properties of the elements, and the nature of molecular bonding? However, their requirements were different from those of the physicists. In 1902 G.N. Lewis proposed, but did not publish, an atomic model with electrons placed at the corners of a cube: single bonds such as the Cl – Cl bond were represented by two cubic atoms sharing a common edge, while in double bonds the two atoms shared a common face (Lewis 1916). In 1904 Abegg suggested that his 'rule of eight' for the maximum sum of electropositive and electronegative valence that an element exhibited, be interpreted as showing that the maximum number of 'points of attack' for bonding electrons in any atom was eight. (Abegg 1904; Jensen 1984). Despite their employment of electrons, once again, we can see here a discontinuity between chemists and physicists, for these, and Lewis' later (1916), theory of bonding as shared pairs of electrons, relied on the spatial arrangements of static electrons to give plausible explanations. Whereas for the physicist spatial arrangement was less significant than the motion within atoms that overcame the repulsive forces between the electrons and imparted some mechanical stability.

Spatial arrangement was less significant, however, if the chemical bond could be considered as an electrostatic one, based on the complete transfer of electrons from one atom to another. Between 1903 and 1921 George Falk, William Noyes,

Harry Fry and Julius Streglitz all pursued such a theory of bonding (Stranges 1982). It worked well for polar and many inorganic compounds, especially when backed up by the evidence of dissociation into charged ions in electrolysis. However, they failed, despite repeated efforts, to isolate charged atoms in non-polar and organic compounds, or to find evidence of the ‘electromers’ predicted by Fry which might have the same atomic arrangement but an opposite allocation of charges, eg. $\text{H}^+ - \text{Cl}^-$ and $\text{H}^- - \text{Cl}^+$ (Fry 1921). These investigations of electrostatic bonding were based largely on Thomson’s atomic model, which became popular in the USA following his visit in 1903 to deliver the Silliman lectures at Yale (Nye 2001).

Thomson’s model, which he first hinted at in his cathode ray paper of 1897, and finally published, fully developed, in *The Corpuscular Theory of Matter* in 1907, is generally known as ‘the plum pudding model’, a label which vastly underrates its sophistication and wide explanatory power (Thomson 1907). Although a typical physicist’s model that relied solely on rapidly moving electrons for its mass, it diverged significantly from other such models which were mainly concerned with explaining atomic spectra (Stranges, 1982). Thomson’s model made little attempt to explain spectra, but exemplified his chemical concerns in offering explanations for bonding, valence, the periodic properties of the elements, and radioactivity. It introduced ideas that are still current today in theories of valence: that of an electron shell structure; that periodicity originates in a repetition of the shell structure; that valence is a function of the completeness of shells; and that the stability of the rare gases results from the completion of an electron shell. The essential features of the model were rapidly rotating rings of electrons moving within a sphere of uniform positive electrification. Thomson used an analogy with Mayer’s magnets to suggest an arrangement of electrons that was both stable and varied periodically as the number of electrons increased. The analogy gave rise, however, to an essential difference between Thomson’s theory and modern theories of valence: although electrons were lost or gained by the outer shell, the periodicity of properties was determined by the arrangements of electrons in the inner shells, ie. across a row in the periodic table the number of outer electrons remained the same, but their stability was decided by the inner electrons (Thomson 1907, pp. 107-110) The mechanical stability of this system depended on the rapid rotation of the rings. Moving electrons radiate energy, however with several thousand electrons Thomson showed that interference reduced radiation to a point where it ceased to be a problem – indeed the eventual collapse of the atom provided a natural explanation for radioactivity, as he suggested to Rutherford:

Now a moving corpuscle is radiating energy so that its velocity is continually falling though very slowly, a time must come although it will be long in coming when the velocity falls below the critical value, the previous arrangement becomes unstable, there is an explosion and some of the parts have their kinetic energy very much increased, in fact they would behave somewhat like radium. (Thomson to Rutherford, 18 Feb. 1904, Cambridge University Library, ADD 7653 T23)

Although this model was largely chemical in its explanatory power, its viability depended crucially on the spatial and charge distribution electron properties that physicists were interested in - the constitution, and number, of electrons were vitally important. In 1904, when he was developing the model and re-analysing Kaufmann's results, Thomson envisaged an electron as the locus of the very small, or even point-like, end of a vortex tube in the ether, the other, much wider, end of which constituted a positive charge (Thomson 1904, pp. 48-49). He envisaged the electromagnetic mass of the electron as being due to the ether bound up in the lines of electric force converging on the point. The positive end of the tube was sufficiently wide that it carried effectively no mass. The aggregation of positive ends could approximate to the sphere of uniform electrification, with the much smaller negative electrons distributing themselves within it, as required by his model.

However, although he had amplified and extended the model by 1907, Thomson had already realised that it faced significant problems (Falconer 1988). In 1906 he had suggested three ways of determining the number of corpuscles in the atom, and undertook the calculations himself (Thomson 1906). Once again, although his atom was largely chemical in its explanatory power, the results he called upon to investigate it were physical, based on the dispersion of light in gases (using Rayleigh's and Ketteler's data), the scattering of x-rays in gases (using Barkla's data), and the absorption of beta rays by gases (using Becquerel's and Rutherford's data). All three methods concurred: the number of electrons in the atom was of the same order as the atomic weight, rather than the thousands Thomson had invoked. This caused three problems for his atom model: with only a handful of electrons, energy loss was high and the atom decayed too fast. This was less important to Thomson, though, than the other two problems. If not from the electrons, where did the mass of the atom come from? And, if mass now had to be ascribed to positive charge, then the positive charge also had to be much more localised than he had envisaged and could not provide a sphere of uniform electrification.

Thomson's response shows him progressively shifting slightly away from his previous commitment to a physicists' electron which provided an explanatory framework for the universe, and towards a more empirical investigation of positive ions. That this shift was a painful one is evident in the opening paragraphs of *The Corpuscular Theory of Matter*. Following his acknowledgement that 'The theory is not an ultimate one; its object is physical rather than metaphysical', he makes his famous justificatory statement that, '... a theory of matter is a policy rather than a creed; its object is to connect or co-ordinate apparently diverse phenomena, and above all to suggest, stimulate and direct experiments' (Thomson 1907, p. 2). His experimental technology, however, remained that in which he had years of expertise: the deflection of gaseous discharge in electric and magnetic fields, although, as with Kaufmann's electron mass experiments, recording of the results was as a visual representation, in this case tracings of the fluorescence at the end of the tube (Falconer 1988).

Positive rays, or ‘Kanalstrahlen’ are ions that stream through a hole in the cathode of a gas discharge tube. By 1907 little was known about them except that they were positively charged and had a charge to mass ratio comparable to that of the hydrogen ion. Thomson experimented on them for the next eight years, initially in the hope of finding evidence for a universal and fundamental positive particle analogous to the electron, despite his doubts that atoms could be decomposed in discharge tubes (Thomson 1907; Falconer 1988). Early results suggested that the hydrogen ion was such a unit, and Thomson turned to investigating the mechanism by which atoms split up and gave out the fundamental ions. This experimental programme ran into an increasing number of problems and inconsistencies, and by 1910 he had quietly abandoned it. Ironically, it was his trial of a physicist’s, quantitative, technology of collecting and measuring the rays using a Faraday cylinder, in 1912, that demonstrated conclusively that the earlier results had been due to hydrogen contamination (Thomson 1912).

This further failure of Thomson’s reductionist, but chemically promising, programme, cleared the way forward for physical chemists and chemical physicists, and freed them from any necessity to conform to the demands of a dynamic electron atom. Once again Thomson, himself, was at the centre of developments. He had taken Francis Aston on as an assistant in 1910. As Aston improved the positive ray apparatus, they began to find evidence, not of universal hydrogen ions, but of ‘characteristic’ atomic and molecular ions corresponding to the gases in the discharge tube, a finding that had an impact both on theories of chemical bonding, and on the experimental technology of chemistry.

As early as 1905 Thomson had suggested that as well as electrostatic bonding, which he called ‘E’ type, directional bonding between uncharged atoms, called ‘M’ type, was possible. At distances of the order of the separation of atoms in molecules, he suggested, there were directional variations in the electric field which depended on the arrangement of the corpuscles in the atom. Along certain directions, even uncharged atoms could bind each other in stable configurations provided they were oriented correctly (Thomson 1905). At the time he believed that most bonding was E type, and reserved M type purely for bonding between identical atoms. However, his quantitative experiments in 1912, counting numbers of characteristic ions with a Faraday cylinder, suggested to him that the atoms within many molecules, such as CO, were uncharged – a conclusion that the American chemists working with chemical methods were not to reach until 1921. Combining his previous bonding theories with ideas he had developed about dipole atoms during his positive ray investigations, Thomson now suggested that most molecular bonding was due to the attraction between dipolar atoms without the transfer of electric charge (Thomson 1912). This bonding, then, began to look remarkably similar to that he had suggested in lectures in Cambridge in 1897, in his earliest work on electrons, before dynamic considerations came into play (see Figure 1). It developed into his 1914 suggestion that two tubes of force were involved in non-

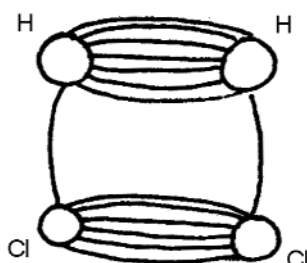


Fig. 1. Sketch of Thomson's 1897 molecular compound, based on notes Rutherford took during Thomson's lectures at Cambridge (Cambridge University Library, Rutherford Collection, ADD 7653 NB4). It shows a single polar hydrogen atom consisting of a large number of vortex tubes and loosely linked by a pair of stray tubes to a single polar chlorine atom.

polar bonds, between an electron of the first atom and the positive part of the second, and between the positive part of the first atom and an electron of the second (Thomson 1914). This suggestion formed one element of G.N. Lewis' fully developed and widely influential static model of the shared electron pair bond (Lewis 1916). The other element, Parson's theoretical discussion of magnetic electrons, arose from Parson's dissatisfaction with the Bohr atomic theory – a typical 'physicist's atom' designed to explain spectra - as a basis for chemical explanation (Parson 1915).

Although his earlier supposition that atoms could not be decomposed in discharge tubes was now confirmed, Thomson had a great investment in discharge as an experimental technology, and was already moving slightly towards a semi-empirical methodology. Theoretically, he began treating the positive part of the atom as an indivisible unit, developing an atomic model consisting of a central core, made up of positive electricity and most of the electrons, surrounded by a few loosely bound valence electrons. Experimentally, he and Aston developed the positive ray deflection methods into a tool for chemical analysis, recording the deflection of characteristic atomic and molecular ions on photographic plates, and publishing lists of ions present during discharge. In 1912 they found the first evidence for non-radioactive isotopes, those of neon, using this method (Thomson 1912). Following up on this discovery after the First World War Aston developed the photographic positive ray tube into the mass spectrograph, while Dempster in Chicago used a different deflection geometry and quantitative measurement by a quadrant electrometer to invent the mass spectrometer (Dempster 1918; Aston 1919). Here, as an unintended consequence of what was essentially a crisis in physics, we finally see the manipulative techniques that made the electron real for physicists, enter into physical chemistry – where perhaps they helped to make isotopes 'real' if not electrons (Falconer 1988; Hughes 1993; Kragh 2000)

Conclusion

I have reviewed briefly the early history of the electron in chemistry and physics considering not only the theoretical role of the electron, but also the experiments surrounding it, and the way the two were intimately connected. In doing so, I have suggested reasons why, perhaps, the electron did not become ‘real’ to chemists, and remained, as Nye has claimed, an organising principle. At the same time, although I adopt Gavroglu’s characterisation of ‘physicist’s’ and ‘chemist’s’ approaches, I question his claim that until the 1920s the ‘electron’ was common to physics and chemistry. I suggest that the very methods of its ‘discovery’ introduced a fracture in how it was perceived in the two fields; while it might be regarded as a potential explanatory principle by both, it was only ‘owned’ by the physicists who had the means to experiment on it.

Between 1905 and 1914, the interplay of these factors is best seen in the work of J.J. Thomson. During this period the physicists’ reductionist programme floundered along a number of fronts: the electromagnetic world view was overtaken and rendered irrelevant by the rise of relativity theory; positive electricity appeared impossible either to dismiss or to reduce to fundamental units; investigations of radioactivity were rapidly increasing the complexity of the elements; and the relationship between atomic structure and spectra seemed solvable only by abandoning the accepted laws of physics. Thomson was one of the few people who was in a position to follow these developments in physics, and had both an interest in chemical explanation, and the experimental means to manipulate electrons. The chemists were heavily reliant on his results and speculations.

By 1914 the power of the physicists’ programme had collapsed and chemists were in a position to assert their own approaches to the role of the electron in bonding. While they might not have the means to manipulate and gain ownership of electrons, they were well able to experiment directly on chemical bonding. At the same time, some of the physicists’ tools began to enter into chemistry as a means of investigating chemical atoms, rather than electrons, although the mass spectrometer was not fully adopted until later when it had become a relatively stable, black box instrument.

Acknowledgements

I would like to thank the Arts Faculty, Open University, UK for research support and encouragement over the last three years.

BIBLIOGRAPHY

- Anon, 1897. Editorial. *The Electrician*, 39, 299.
- Abegg, R., 1904. Die Valenz und des periodische System. Versuch einer Theorie der Molekülverbindungen. *Zeitschrift für anorganische Chemie*, 39, 330.
- Abraham, M., 1902. Dynamik des Elektrons. *Nachrichten von der Gesellschaft der Wissenschaften zu Göttingen. Mathematisch-Physikalische Klasse*, 4, 20-41.
- Arabatzis, T. and K. Gavroglu, 1997. The chemists' electron. *European Journal of Physics*, 18, 150-163.
- Aston, F.W., 1919. The constitution of the elements. *Nature*, 104, 393.
- Carazza, B. and N. Robotti, 1996. The first molecular models for an electromagnetic theory of dispersion and some aspects of physics at the end of the nineteenth century. *Annals of Science*, 53, 587-607.
- Chayut, M., 1991. J.J. Thomson, the discovery of the electron and the chemists. *Annals of Science*, 48, 527-544.
- Clausius, R., 1857. On the nature of the motion which we call heat. *Philosophical Magazine*, (4) 14, 108-127.
- Crookes, W., 1886. Presidential Address. *Reports of the British Association*, 558-576.
- Dempster, A.J., 1918. A new method of positive ray analysis. *Physical Review*, 11, 316-324.
- Ebert, H., 1893. Electricische Schwingungen molecular Gebilde. *Annalen der Physik*, 49, 651-772.
- Ebert, H., 1894. Heat of dissociation according to the electrochemical theory. *Philosophical Magazine*, (5) 38, 332-336.
- Falconer, I., 1985. Theory and experiment in J.J. Thomson's work on gaseous discharge. Unpublished PhD thesis, University of Bath, UK.
- Falconer, I., 1987. Corpuscles, electrons and cathode rays, J.J. Thomson and the 'discovery of the electron'. *British Journal for the History of Science*, 20, 241-276.
- Falconer, I., 1988. J.J. Thomson's work on positive rays. *Historical Studies in the Physical Sciences*, 18 (2) , 265-310.
- Falconer, I., 2001. Corpuscles to Electrons, in *Histories of the Electron*. (J.Z. Buchwald and A. Warwick eds.). MIT Press, Cambridge, Mass, 77-100.
- Fry, H., 1921. The electronic conception of valence and the constitution of benzene. Longmans Green & Co, London.
- Gavroglu, K., 1997. Philosophical issues in the history of chemistry. *Synthese*, 111, 283-304.
- Gavroglu, K., 2001. The physicists' electron and its appropriation by the chemists, in *Histories of the electron*. (J.Z. Buchwald and A. Warwick eds.). MIT Press, Cambridge, Mass, 363-400.
- Hacking, I., 1983. Representing and intervening, introductory topics in the philosophy of natural science. Cambridge University Press, Cambridge.
- Hertz, H., 1883. Versuche über die Glimmentladung. *Annalen der Physik und Chemie*, 19, 782-816.
- Hertz, H., 1886. Über sehr schnelle elektrische Schwingungen. *Annalen der Physik*, 31, 421, 543.
- Hon, G., 1995. Is the Identification of Experimental Error Contextually Dependent?, The Case of Kaufmann's Experiment and its Varied Reception. In: *Scientific Practice*. (J.Z. Buchwald ed.). Chicago, University of Chicago Press, 170-223.
- Hughes, J., 1993. *The Radioactivists, Community, Controversy and the Rise of Nuclear Physics. History and Philosophy of Science*, Cambridge.
- Jensen, W.B., 1984. Abegg, Lewis, Langmuir and the octet rule. *Journal of Chemical Education*, 61, 191-200.
- Kaufmann, W., 1897. Die magnetische Ablenkbarkeit der Kathodenstrahlen. *Annalen der Physik*, 61, 544-52.

- Kaufmann, W., 1901. Die magnetische und elektrische Ablenkbarkeit der Becquerelstrahlen und die scheinbare Masse der Elektronen. Nachrichten von der Gesellschaft der Wissenschaften zu Göttingen. Mathematisch-Physikalische Klasse, 3, 143-55.
- Kaufmann, W., 1902. Über die elektromagnetische Masse des Elektrons. Nachrichten von der Gesellschaft der Wissenschaften zu Göttingen. Mathematisch-Physikalische Klasse, 4, 291-296.
- Kolacek, F., 1887. Versuch einer Dispersionserklärung vom Standpunkte der electromagnetische Lichttheorie. Annalen der Physik und Chemie, 32, 224-255.
- Kragh, H., 1982. Julius Thomsen and 19th-century speculations on the complexity of atoms. Annals of Science, 39, 37-60.
- Kragh, H., 2000. Conceptual changes in chemistry, the notion of a chemical element, ca. 1900-1925. Studies in History and Philosophy of Science Part B, Studies in History and Philosophy of Modern Physics, 31 (4) , 435-450.
- Larmor, J., 1894. A dynamical theory of the electric and luminiferous medium. Part 1. Philosophical Transactions of the Royal Society, 185, 719-822.
- Larmor, J., 1895. A dynamical theory of the electric and luminiferous medium. Part 2. Philosophical Transactions of the Royal Society, 186, 695-743.
- Larmor, J., 1897. A dynamical theory of the electric and luminiferous medium. Part 3. Philosophical Transactions of the Royal Society, 190, 205-300.
- Lelong, B. 2001. Paul Villard, J.J. Thomson, and the composition of cathode rays , in Histories of the electron. (J. Z. Buchwald and A. Warwick eds.). MIT Press, Cambridge, Mass, 135-167.
- Leone, M. and N. Robotti. 2000. Stellar, solar and laboratory spectra, the history of Lockyer's protoelements. Annals of Science. 57 (3), 241-266.
- Lewis, G. N., 1916. The atom and the molecule. Journal of the American Chemical Society, 38, 762-785.
- Lockyer, N. 1881. Solar physics, the chemistry of the sun. Nature, 24, 267, 296, 315, 391.
- Lorentz, H.A., 1878. Over het verband tusschen de vootplantings snelheid en samstelling der middenstoffen. Verhandelingen der Koninglijke Akademie van Wetenschappen, Amsterdam, 18, 1.
- Maxwell, J.C., 1860. Illustrations of the dynamical theory of gases. Philosophical Magazine (4) 19, 19-32; (4) 20, 21-37.
- Nye, M.J., 2001. Remodeling a classic, the electron in organic chemistry , in Histories of the electron. (J.Z. Buchwald and A. Warwick eds.). MIT Press, Cambridge, Mass, 339-361.
- O'Hara, J.G., 1993. George Johnstone Stoney and the conceptual discovery of the electron. Stoney and the Electron. Dublin, Royal Dublin Society, 5-28.
- Parson, A.L., 1915. A magneton theory of the structure of the atom. Smithsonian Miscellaneous Collections, (6) 11, 1-80.
- Perrin, J., 1895. Nouvelles proprietes des rayon cathodiques. Comptes Rendus, 121, 1130.
- Plucker, J., 1858. Poggendorf Annalen, 105, 84.
- Rayleigh, R.L., 1942. The life of Sir J.J. Thomson. Cambridge University Press, Cambridge.
- Richartz, M.F., 1891. Sitzungsberichte der Niederrhein Gesellschaft zu Bonn, reported in Ebert 1894.
- Schuster, A., 1890. The discharge of electricity through gases Royal Society Bakerian Lecture. Proceedings of the Royal Society, A 47, 526-559.
- Schuster, A., 1894-5. The kinetic theory of gases. Nature, 51, 293.
- Searle, G.F., 1897. On the motion of an electrified ellipsoid. Philosophical Magazine, 44, 323-341.
- Stoney, G.J., 1874. On the physical units of nature. British Association Reports, 22.
- Stoney, G.J., 1881. On the physical units of nature. Philosophical Magazine, (5) 11, 381-390.
- Stoney, G.J., 1891. On the cause of double lines and of equidistant satellites in the spectra of gases. Transactions of the Royal Dublin Society, (2) 4, 563-608.

- Stranges, A.N., 1982. *Electrons and valence, development of the theory, 1900-1925*, Texas A & M University Press.
- Thomson, J.J., 1883. *Treatise on the motion of vortex rings*. Macmillan, London.
- Thomson, J.J., 1893. *Notes on recent researches in electricity and magnetism*. Clarendon Press, Oxford.
- Thomson, J.J., 1894. The connexion between chemical combination and the discharge of electricity through gases. *British Association Reports*, 482-493.
- Thomson, J.J., 1895. A method of comparing the conductivity of badly conducting substances. *Proceedings of the Cambridge Philosophical Society*, 8, 258-269.
- Thomson, J.J., 1895. The relation between the atom and the charge of electricity carried by it. *Philosophical Magazine* 40, 511-527.
- Thomson, J.J., 1897a. Cathode Rays. *Philosophical Magazine*, (5) 44, 293-316.
- Thomson, J.J., 1897b. Cathode rays. *Royal Institution Friday Evening Discourse*, 30 April. *The Electrician*, 39, 21 May, 104-109.
- Thomson, J.J., 1904. *Electricity and Matter*. Silliman Lectures at Yale University. Archibald Constable & Co, Westminster.
- Thomson, J.J., 1905. The structure of the atom. *Royal Institution of London, Notices of Proceedings* 18, 49-63.
- Thomson, J.J., 1906. On the number of corpuscles in an atom. *Philosophical Magazine*, (6) 11, 769-778.
- Thomson, J.J., 1907. *The Corpuscular Theory of Matter*. London, Constable.
- Thomson, J.J., 1907. On rays of positive electricity. *Philosophical Magazine*, (6) 13, 561-575.
- Thomson, J.J., 1912. Further experiments of positive rays. *Philosophical Magazine*, (6) 24, 209-253.
- Thomson, J.J., 1914. The forces between atoms and chemical affinity. *Philosophical Magazine*, (6) 27, 257-89.
- Villard, P., 1898. Sur les rayons cathodiques. *Comptes Rendus*, 126, 1564-1566.
- Villard, P., 1908. *Les rayons cathodiques*. Gauthier-Villars, Paris.
- Wiechert, E., 1897. Ergebnis einer Messung der Geschwindigkeit der Kathodenstrahlen. *Schriften der Physikalisch-Ökonomisch Gesellschaft zu Königsberg*, 38, 3-16.
- Zeeman, P., 1896. On the influence of magnetism on the nature of the light emitted by a substance. Part 1. *Communications from the Physical Laboratory at the University of Leiden*, 33, 1-8.