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A parabolic curve. The changing attitude of British physicists towards chemistry, 1860-1930

Summary - The present research studies the changing attitude towards chemistry of six British physicists, viz. Maxwell, Kelvin, Rayleigh, J.J. Thomson, Rutherford and Dirac. The principal historiographical assumptions are that a great scientist is representative of a style of research and at once is conditioned by - and conditions - the ethos of his professional community. The disciplinary relationship between physics and chemistry changed deeply in time, with the scientific leaders' attitude which went from indifference (Maxwell) to interest (Rayleigh, J.J. Thomson), and again to indifference (Rutherford and Dirac). The changing attitude of Kelvin is particularly interesting, because he passed from a strong criticism to an explicit appreciation. The causes of this shifting orientation are various, but probably the changing epistemological feelings are the most important. Maxwell and Dirac were far in time, but near in the certainty that physics could solve any problem of the real world. For them, chemistry was of no interest. In a very different disciplinary climate, the attitude of Maxwell and Dirac was shared also by Rutherford. Kelvin, Rayleigh and Thomson lived the crisis of the classical physics in a period in which the classical chemistry was strong and still flourishing. Their epistemological awareness was an important source of their interest in chemical affairs.

Keywords: Maxwell, Kelvin, Rayleigh, Thomson, Rutherford, Dirac

The relationship between the different scientific activities was object of philosophical reflection since antiquity, however since the first decades of the Nineteenth Century, the issue assumed a much more concrete (academic) interest because the process of specialization brought in evidence the fact that the ideal figure of 'natural philosopher' had begotten several different figures of 'scientist', the physicist, the chemist, and so on. Through the twin processes of professionali-

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sation and specialisation of the practitioners, the different scientific disciplines became 'visible' to scientists of any kind.

In the present research, I intend to follow the changing attitude towards chemistry of six British physicists, viz. Maxwell, Kelvin, Rayleigh, J.J. Thomson, Rutherford and Dirac. My principal historiographical assumptions are that a great scientist is representative of a style of research and at once is conditioned by – and conditions – the *ethos* of his professional community.

In several previous contributions I studied the attitude towards chemistry of Maxwell [8] and Kelvin [13], the direct involvement of Thomson in chemical questions [9, 11], some aspects of the cultural state of affairs of British chemistry in the second half of the Nineteenth Century, [3-5] and the different approach to the corpuscular world by physics and chemistry in the central part of the Nineteenth Century [6]. Since the present research regards a long period, I will sometime refer to these previous contributions in order to support my claims.

Before the narrative part of the present research, I have to clarify a couple of methodological points. The word lattitudel has a twofold meaning. One meaning points to an intellectual activity: 'attitude' is "the way that you think and feel about somebody or something"; the other meaning points to a realized action: 'attitude' is "the way that you behave towards somebody or something that shows how you think and feel" (Oxford Advanced Lerner's Dictionary, ad vocem). From this point of view, our six physicists had attitudes towards chemistry with a very different balance between the two components of thought and action. The second methodological point can be expressed by two similar but not always clearly distinct terms: epistemic vs. epistemological. I will label as 'epistemic' a theoretical or practical activity aimed to gain specific knowledge (not necessarily 'scientific' knowledge) about a particular thing. These epistemic activities are realized in laboratories or at desks as 'knowledge procedures'. Looking again at the Dictionary, we see that a 'procedure' is a "way of doing something, especially the usual or correct way". I like to use this term in order to stress the 'legal' or 'collective' side of the scientists' behaviour. I will limit the use of 'epistemological' for referring to a theoretical activity that has as object the knowledge of something. In short, 'epistemic' refers directly to knowledge procedures, and 'epistemological' refers to the reflection about the knowledge activities and the resulting knowledge.

JAMES CLERK MAXWELL: THE IMMUTABILITY OF MOLECULES

Few scientists have attracted the attention of science historians more than James Clerk Maxwell (1831-1879). Not only his immense contribution to physical theory has been examined in any details, but also his attitude towards hot themes as Darwinism. Nowadays, this last issue is a frequent topic of discussion on the creationist side of the Christian fundamentalism, however the same Maxwellian texts always quoted by creationists [40-41] may be analysed by our actual point of view

[8]. Here I will focus on Maxwell's curious stance about Avogadro's Law and on the exhibited referential opacity of the word latom and molecule in Maxwell's scientific discourse.

AVOGADRO IN DISGUISE

The vicissitudes of Avogadro's hypothesis in the Nineteenth Century are well known [7]. Maxwell's contribution to establish an acceptable status to this hypothesis was not inconsiderable; nevertheless, the textual traces that we find in his writings testify several actual misconceptions of the great scientist. The principal references of Maxwell to Avogadro's law are in the fundamental papers on the kinetic theory of gases published in 1860 [42] and in 1867 [43].

Maxwell presents his first contribution to the kinetic theory of gases as a collection of 24 exercises in a new brand of mathematical physics. It is in the solution of the twelfth problem, "To find the pressure on unit of area of the side of the vessel due to the impact of the particles upon it", that we find the reference to Avogadro's law:

"*N*, the number of particles in unit of volume, is the same for all gases at the same pressure and temperature. This result agrees with the chemical law, that equal volumes of gases are chemically equivalent" [42].

It is obvious that did not exist (and it does not exist altogether now) a 'chemical law' as that which Maxwell is referring to. In reality, the great physicist is referring to the law of Gay-Lussac on the reactivity of gases. The reference becomes clearer, together with Maxwell's misconceptions, in the article published seven years later. In this paper Avogadro's law has a much more important epistemological role that in the 1860 paper. At the end of the 40 lines of introduction, the Author states his knowledge intentions and the awaited results:

"I propose in this paper to apply this theory to the explanation of various properties of gases, and to shew that, besides accounting for the relations of pressure, density, and temperature in a single gas, *it affords a mechanical explanation of the known chemical relation between the density of gas and its equivalent weight, commonly called Law of Equivalent Volumes.* It also explains the diffusion of one gas through another, the internal friction of a gas, and the conduction of heat through gases" [43].

I have used italics in order to emphasize two facts, that Maxwell gives a central role to Avogadro's law and that once more our Author misses the target. Maxwell trays to give a "mechanical explanation" to a "chemical relation" (actually the Gay-Lussac's law), which is not deducible from Avogadro's law without further conjectures on the atomic constitution of molecules. To be sure, Avogadro's law is not at all a 'chemical law'; in the course of the article Maxwell states the law: "equal volumes of different gases at equal pressures and temperatures contain equal numbers of molecules", and later, eventually, the reader may know the name of the alleged author of such an important law:

"[T]he masses of the individual molecules are proportional to the density of the gas. This result, by which the relative masses of the molecules can be deduced from the relative densities of the gases, was first arrived at by Gay-Lussac from chemical considerations. It is here shewn to be a necessary result of the Dynamical Theory of Gases" [43].

A scientist is not obliged to know the history of science, but he has to control his epistemic statements: neither Avogadro's law nor Gay-Lussac's law may be deduced "from chemical considerations". Moreover, a scientist of the stature of Maxwell is always careful not to say silly words on scientific issues of great importance; so, a simple explanation of the careless epistemic behaviour of Maxwell is the undervaluation of what is actually a "chemical relation", i.e the relationship between the reciprocal reactivity of substances.

Referential opacity and theology of nature

Maxwell gave much more emphasis to his deduction of the Avogadro's law in 1867 than in 1860; he felt this law as a 'chemical' law, so – indirectly – he reveals that chemistry, as a discipline, was increasing in interest. Several other proofs of his perception of the increasing importance of chemistry can be found in his address to the British Association for the Advancement of Science (BAAS) of 1873. The first, unambiguous proof is what he says about the crucial word, which titles his address: "Molecule is a modern word. [...] The ideas it embodies are those belonging to modern chemistry". A second proof is given in the following passage:

"The dynamical theory also tells us [...] that, on an average, every molecule, great or small, will have the same energy of motion. The proof of this dynamical theorem, in which I claim the priority, has recently been greatly developed and improved by Dr Ludwig Boltzmann. The most important consequence which flows from it is that a cubic centimetre of every gas at standard temperature and pressure contains the same number of molecules. This is the dynamical explanation of Gay Lussac's law of the equivalent volumes of gases" [41].

In 1873, the *most important consequence* of the theorem of equipartition of energy is Avogadro's law (as usual here disguised as Gay-Lussac's law). However, in Maxwell's address we find another kind of proof, on his faulty conception of what is a molecule:

"Every substance, simple or compound, has his own molecule. If this molecule be divided, its parts are molecules of a different substance or substances from that of which the whole is a molecule. An atom, if there is such a thing, must be a molecule of an elementary substance. Since, therefore, every molecule is not an atom, but every atom is a molecule, I shall use the word molecule as the more general term" [41].

With this semantic choice, Maxwell condemns his discourse on the corpuscular world to a permanent and always impending referential opacity. Following Quine we say that two terms are referentially opaque if they cannot be substituted *salva veritate* (i.e. without changing the truth value of the statement). In our context, an immediate consequence of this opacity can be seen in the same paper we are discussing. At the end of the printed address is appended a "Table of Molecular data", in which the mass of the hydrogen molecule is 1, and the relative masses are 16 for the oxygen molecule, 14 for carbon oxide and 22 for carbon dioxide; these values cannot justify in any way the formulae of a following "Table of Diffusion": H, O, CO, CO₂ [41].

With his contributions to statistical mechanics, Maxwell gave powerful means of study of the molecular world, and it is ironic that he held loose or fault ideas on the objects of his research – the molecules. For brevity sake, I limit myself to couple of textual examples.

Speaking before the members of the London Chemical Society, on 18 February 1875, Maxwell extols the 'dynamical' deduction of Avogadro's law ("the most important application which has yet been made of dynamical methods to chemical science" [44]) and clearly sets up two different epistemic 'purities':

"This result coincides with the law of equivalent volumes established by Gay Lussac. This law, however, has hitherto rested on *purely chemical evidence*, the relative masses of the molecules of different substances having been deduced from the proportions in which the substances enter into chemical combination. It is now demonstrated on dynamical principles. The molecule is defined as that small portion of the substance which moves as one lump during the motion of agitation. This is a *purely dynamical definition*, independent of any experiment on combination" [44].

I suspect that an epistemic 'purity' is very rare, and perhaps it exists only in mathematics, but in Maxwell's discourse, what is strange is the 'dynamical' definition of molecule "as one lump". In English llumpl is a "hard or compact mass, usually without a regular shape" (*a lump of clay*). A similar shapeless 'object' is far from any 'chemical' or 'dynamical' representation of a molecule.

There were many cultural obstacles between Maxwell scientific creativity and the chemical molecule, the molecule constructed in laboratory and described with accurate molecular maps. Sure enough, the obscurity which envelopes Maxwell's molecule has several sources, and the liberal education and natural theology are the most important [8]. The recurring Maxwell's attributes of molecules are: "one and indivisible, unalterable by any power in nature" [45], "imperishable and unalterable and perfectly similar [...] of exactly the same mass [...] vibrating in exactly the same time" [45], "absolutely unalterable [...] absolutely identical", "indestructible" [41]. In the entry "Atom", printed in 1875, we read:

"[T]he individual molecules neither are born nor die, they have neither parents nor offspring [...]. If we suppose that the molecules known to us are built up each of some moderate number of atoms, these atoms being all of them exactly alike, then we may attribute the limited number of molecular species to the limited number of ways in which the primitive atoms may be combined so as to form a permanent system" [40].

We are reading the most important text for the understanding of Maxwell's natural theology. For Maxwell "the individual molecules" were the result of an act of supernatural creation; behind such a theological obstacle, the great physicist could not see the endless constructive ability of chemistry.

WILLIAM THOMSON, FIRST BARON KELVIN OF LARGS: A CHANGE OF MIND

The dramatic and untimely death of Maxwell deprived molecular science of a great, creative scientist. Maxwell was seven years younger than Lord Kelvin (1824-1907), another formidable theoretician who lived enough to see and participate in the exciting developments in physics and chemistry, which happened in the last decade of the Nineteenth Century and in the first decade of the Twentieth Century. (In the text of the following pages I will always refer to William Thomson as 'Lord Kelvin', also when the title results anachronistic). Kelvin's abundant scientific and popular production let us follow his intellectual journey from a critical stance on the chemical theories to an attitude of appreciation and praise.

Kelvin and chemistry, first phase

In April 1862, Kelvin read a short paper before the Royal Society of Edinburgh. The title regarded two intriguing actions, respectively very general and very particular [86]; this was a kind of intellectual exercise that always interested Kelvin. At the end of the paper, the Author gives his epistemological judgement on the validity of chemical theories:

"Physical science abounds with evidence that there is an ultimate very intense heterogeneousness in the constitution of matter. All that is valid of the unfortunately so-called 'atomic' theory of chemistry seems to be an assumption of such heterogeneousness in explaining the combination of substances. [...] whatever is assumed to be the structural character of a chemical compound, a dynamical law of affinity [...] must be added to what some writers seem to suppose done by their 'atomic theory'" [86].

With few words, Kelvin disposes of the valence theory and of the structural approach in organic chemistry. Looking at the date of this contribution, 1862, we can mention that the Austrian physicist Loschmidt had published in 1861 a booklet in which he presented the structural formulae of 368 compounds [39].

Kelvin seems certain that the chemists' alleged theories are not at all theories. This attitude is spontaneous in a mathematical-physicist as Kelvin (or Maxwell), and it is Kelvin's great worth the fact that he changed his opinion, if not on the 'chemical theories' at least on the chemist's astonishing results. However, the intellectual journey was long, with many stopping places. In one of this stops Kelvin played with a beautiful physical-mathematical toy proposed by the 'omniscient' Helmholtz – the indestructible vortex, which in Kelvin's hands became the 'vortex atom'. In the introductive lines of Kelvin's famous paper on the vortex atom the Author takes up his position against the classical-chemical atom:

"[T]he 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" [87].

This general condemnation was written in 1867. A more specific disapproval of chemical theories was published three years later, in March 1870, in the introductory paragraph of the paper on "The Size of Atoms":

"Chemistry is powerless to deal with this question [of the size of atoms], and many other of paramount importance, if barred, by the hardness of its fundmental assumptions, from contemplating the atom as a real portion of matter occupying a finite space, and forming a not immesurably small constituent of any palpable body" [88].

Here is apt to recall that in 1870 the researches of chemists on the *atomic volumes* had given good results, and that in few month after Kelvin's essay these results should be elaborated by Lothar Meyer to supply the most evident (visible) experimental base of the periodic system of elements [47]. It is evident that the great scottish physicist ignored the chemical side of the question; he was in the same situation in August 1871, when he repeated the same judgment in the Presidential Address to the BAAS [89]. Kelvin did not revise his opinion also many years later, because he reprinted the 1870 paper on the atomic size in the second volume of the *Treatise on Natural Philosophy*, published in 1890. It is evident too, that the topic forced Kelvin's usual perspicacity into a kind of epistemic deafness. In 1883 he spoke on the size of atoms before the audience of the Royal Institution, and after few introductory words said:

"The chemists do not know what is to be the atom; for instance, whether hydrogen gas is to consist of two pieces of matter in union constituting one molecule, and these molecules flying about; or whether single molecules each indivisible, or at all events undivided in chemical action, constitute the structure" [90].

To tell the truth, Kelvin was in serious difficulty while he was preparing the lecture, because of certain problems of calculation on the relationship between refractive dispersion and the molecular structure of matter [57]. In other terms, he was concerned about his physical-mathematical instrumentation, and the quoted passage was the result of a kind of epistemological automatism: the chemists did not know what was to be the atom. We will see in the next section that this automatism was at its end.

Kelvin and chemistry, second phase

In the autumn of 1884 Kelvin held in Baltimore the famous series of lectures whose text he wrote, re-wrote and greatly extended in the following *twenty* years [35]. Kelvin accurately dated any addendum, so in many respects the *Baltimore Lectures* are a kind of scientific diary on the lasting research of the Author on the molar/molecular issues. The actual lectures in Baltimore were a long *divertissement théâtral*, sometimes exhausting for the excellent pupils but never for the teacher. During the *divertissement*, Kelvin proposed at least eight different models of molecules, described and calculated with the methods of mathematical physics, or material, as a ponderous "wave machine".

The first traces of Kelvin's changing of mind are in a speech given by him in an important occasion in 1885, the opening of the Physical and Chemical Laboratories of the University College of North Wales. Kelvin notes "A chemical laboratory has now become indispensable in all universities", and adds a eulogy of Liebig. At this point, he exclaims:

"If Liebig's laboratory, looking as an old stable, brought out such results to astonish and benefit the world, what must we expect of the beautiful laboratory in which we are now met?" [91].

After the overdue acknowledgement of the astonishing results of chemistry, Kelvin can equate the epistemological value of chemistry and physics:

"[T]here is no philosophical division whatever between chemistry and physics. The distinction is that different properties are investigated by different sets of apparatus. The distinction between chemistry and physics must be merely a distinction of detail and of division of labour" [91].

The phrase "division of labour" belong to the economic register of discourse; it is a sign that Kelvin felt that the chemical benefits to the world were not only humanitarian. Later, towards the end of the century, Kelvin's approach to chemistry became faster.

The discovery of the electron was announced by J.J. Thomson during the course of his evening lecture to the Royal Institution on 30 April 1897. On 21 May Kelvin spoke before the same audience about contact electricity; the day after he sent a letter to Nature in which he accept "an atomic theory of electricity", "Indeed, Faraday's law of electro-chemical equivalence seem to necessitate something atomic in electricity, and to justify the very modern name *electron*". In the short note, he proposes a very interesting model of electrolysis "adopting the essentials of Aepinus' theory, and dealing with it according to the theory of father Boscovich" [33]. Two remarks on this paper must be added: for the present (1897), it is noteworthy that he does not mention the experimental discovery of the electron by Thomson; for the past (1870), we can read a passage of the seminal paper on the size of atoms: "I have no faith whatever in attraction and repulsions acting at a distance between centres of force according to various laws" [89]. Kelvin changed opinion also on the atom

of Democritus and Epicurus; he felt himself "forced" to accept an atomic model similar to the classic one and in this occasion praises Lucretius as the "majestic poetic expositor" of the Greek philosophers [34].

Kelvin's most intense attention on chemical problems is found in one of his most famous contribution, written in 1901 and published on the *Philosophical Magazine* in March 1902. In the rightly celebrated "Aepinus Atomized", Kelvin erases a part of his past epistemological attitude. For example, he speaks of "the binary combinations of two atoms of identical quality which the chemists have discovered in diatomic gases (O_2 , N_2 , &c.)" [36], and so he overturns his statement of 1883 (*vide supra*). Kelvin says to be not completely at ease with his new atomic model based on the 'electrions':

"We might be tempted to assume that all chemical action is electric [...]; but we can feel no satisfaction in this idea when we consider the great and wild variety of quality and affinities manifested by the different substances or the different 'chemical elements'; and as we are assuming the electrions to be all alike, we must fall back on Father Boscovich, and require him to explain the difference of quality of different chemical substances by different law of force between the different atoms" [36].

Even though rhetorically uneasy, the old scientist gives several examples of his creativity. Here is the most 'chemical', formidable statement:

"The complexity of the hydrocarbons and the Van't Hoff and Le Bell of the asymmetric results (chirality) produced by the quadrivalence of carbon makes it probable that the carbon atom takes at least four electrons to neutralize it electrically" [36].

A final essential point is the research program that Kelvin sees open before theoretical physics:

"[T]he suppositions we have made [...] seem to open the way to a very definite detailed dynamics of electrolysis, of chemical affinity, and of heat of chemical combination" [36].

This research program is a chemical program; perhaps it might seem also a plane of invasion, but now, at the beginning of the Twentieth Century, Kelvin fully respects the knowledge endeavour of the chemists. On 23 October 1904, in the course of a prize-given of students he said: "Anything that crystallizes may be made by the chemist" [74], a phrase half admiring, and half resigned.

The reasons for a similar change of mind are surely neither simple, nor evident. In the first place, we must accept Kelvin as an important witness of the rising scientific and academic prestige of chemistry in the second half of the Nineteenth Century. In the second place, I can mention that Kelvin began a demanding political activity in the same period of his 'conversion' towards chemistry [13]. It is well known that in the last decades of the Nineteenth Century the ruling class of the United Kingdom became (slowly) conscious of an economic and military 'overtaking' by the German Empire. The possible connection between personal scientific stance and political concern finds a substantial support in the splendid research by Smith and Norton Wise. Their thesis is proposed in these words: "We seek to show, concretely and in detail, how the science that Thomson produced was inseparably integrated with the industrial culture that he represented" [57]. The changing of Kelvin's mind accompanied in time the rising, strategic importance of the chemical industry and the increasing social-economic role of academic chemistry.

JOHN WILLIAM STRUTT, THIRD BARON RAYLEIGH: THE CHALLENGER

In our small sample of great scientists John William Strutt, third Baron Rayleigh (1842-1919) occupies a special place, not only for the enormous number of published articles (more than 450), but also because he was a very accurate and prolific experimentalist in various fields of physics and chemistry. He first met chemistry in youth, or better still, he met science through a chemical process: photography [28]. Another particular – albeit well known – trait of the scientific life of Rayleigh is that the major part of his experimental researches was conducted outside any academic institution, in his manor at Terling. In the spring of 1873 J.W. Strutt succeeded to the title, and took up residence at Terling, the family manor [56]. For simplicity sake, in the following pages I will use only the name 'Rayleigh'.

The first 'serious' interest in chemistry was born in Rayleigh mind from the theoretical side of the discipline. In 1882 he was chairman of Section A of the BAAS, and he addressed the Section at the Southampton meeting of that year, with a speech entirely dedicated to his epistemological views about physics. At the end of his address, Rayleigh states "It would be an interesting, but too difficult and delicate a task, to enumerate and examine the various important questions which remain still undecided from the opposition of direct and indirect evidence" [59]. He mentions two questions at all, and the second one regards Prout's law, that our Author presents with this words: "according to which the atomic weights of the elements, or at any rate of many of them, stands in simple relation to that of hydrogen". Some chemists "reprobated strongly the importation of *à priori* views into the consideration of the question", but others, impressed by the "close approximations to simple numbers", judge the problem completely open:

"[They] consider that the experimental evidence against simple numbers is of a very slender character, balanced, if not outweighed, by the *à priori* argument in favour of simplicity" [59].

In Rayleigh's (erroneous) opinion, the chemists of this second kind are "more alive to the inevitable imperfections of our measurements", and our physicist begins to feel himself at home with the problem:

"The subject is eminently one for further experiment; and as it is now engaging the attention of chemists, we may look forward to the settlement of the question by the present generation. The time has perhaps come when a redetermination of the densities of the principal gases may be desirable" [59].

In the course of the same address, Rayleigh had affirmed a bold – if not overconfident – epistemological rule:

"The door of experiment stands always open; and when the question is ripe, and the man is found, he will nine times out of ten find it necessary to go through the work again" [59].

Rayleigh's long involvement in the determination of atomic weights began in this mood of curiosity and dispute. It is well known that this involvement led the great physicist to the discovery of the anomalous density of the 'atmospheric' nitrogen in comparison with the density of the 'chemical' nitrogen. The 'collaboration' with William Ramsay led to a joint paper in which Rayleigh and Ramsay announced and at length gave data on the discovery of argon, the first noble gas [38]. For the history of the discovery of argon we have many primary and secondary sources, here I will focus on two different themes, one more general and one more particular: Rayleigh's engagement with the problems of atomic weights determination and Rayleigh's competition with Ramsay.

Rayleigh and the determination of atomic weights

The strategy of Rayleigh for determining some fundamental atomic weights relied completely upon the measurement of gas densities. In the course of more than two decades, Rayleigh measured the density of hydrogen, oxygen, nitrogen, carbon dioxide, carbon oxide, nitrous oxide and – of course – argon.

Rayleigh was very suspicious of the usual chemical procedures, and from this point of view, he was willy-nilly thinking as a chemist. In 1900, he published a very short note on the weight of gaseous hydrogen desiccated by liquid air. The core of his argument is this:

"[T]he object was not so much to make a new determination of the highest possible accuracy, as to test whether any serious error could be involved in the use of phosphoric anhydride, such as might explain the departure of the ratio of densities of oxygen and hydrogen from that of 16:1. I may say at once that the result was negative" [68].

Rayleigh went well inside the chemical territory, for example when looked for the impurity that he thought to be present in the nitrogen obtained from urea [67]. In some contrast with this critical attitude towards the chemical procedures, Rayleigh began and continued the measurement of gas density for a somewhat long time assuming that Avogadro's law was valid for any gas, and in any condition of temperature and pressure. The contrast is meaningful, even more because Rayleigh knew perfectly the theory of real gases of Van der Waals. In 1891, he published on *Nature* two letters in which he defended Van der Waals against the critics of Tait [61], and in 1892, he used Van der Waals' theory in a study of the surface forces [62]. In the first paper on the determination of the relative densities of hydrogen and oxygen, Rayleigh wrote: "If [the] investigations are conducted with gases under the normal atmospheric conditions as to temperature and pressure, any small departures fro the laws of Boyle and Charles will be practically without influence upon the final number representing the ratio of atomic weights" [60]. In the second paper on the same problem Rayleigh only hints in a footnote at "the applicability of Avogadro's law to very rare gases" and at "the formula of Van der Waals" [63]. In 1904 Rayleigh returned on the problem: "I hope shortly to be in a position to apply the correction which will allow us to infer what is the ratio of molecular weights according to Avogadro's rule" [71]. When, at last, he had applied the "correction for carbonic acid after Van der Waals", he preferred to use the 'reduced' form of Van der Waals' equation proposed by the French physicist Daniel Berthelot [72].

The long series of researches on gas densities gave Rayleigh and the scientific community several meaningful results. The first was negative and personal, insomuch he tacitly renounced to Prout's hypothesis. As we saw above, still in 1900 Rayleigh was trying to "explain the departure of the ratio of densities of oxygen and hydrogen from that of 16:1", but in the last and definitive paper of 1905 Prout is no more mentioned. In this important article, the accent is put on the atomic weight of nitrogen obtained in 1894 with Ramsay: "The uncorrected number for nitrogen (14.003 corresponding to O=16) has already been given [38], and contrasted with the 14.05 obtained by Stas. This question deserves the attention of chemists" [72]. In reality, then the problem of the nitrogen atomic weight was in discussion in the International Committee on Atomic Weights, and Rayleigh's contribution (to his satisfaction) is quoted in the 1906 Report, together with those of three other researchers [14]. Finally, it is to be mentioned that Rayleigh made the researches on gases at low pressure using very precise manometers of his own innovative design [70]. Thus, Rayleigh confirmed his fame of excellent experimenter also in the researchers on gas densities, both for the instruments and for the results.

Rayleigh vs. Ramsay

The 'collaboration' between Rayleigh and Ramsay was in some senses forced; it was analysed in many details [27], but in our context the most interesting feature is the competition engaged by the excellent physicist on the quantitative preparation of argon. The quantitative isolation of a pure substance is a strictly chemical operation, and in this sense, Rayleigh challenged Ramsay on his own ground. The competition developed on two dissimilar methods. Rayleigh used the 'oxygen method', which went back to Cavendish, and which consisted in the oxidation of nitrogen by the help of an electrical discharge, followed by the removal of the nitrogen oxides. Ramsay used the 'magnesium method', in which nitrogen is directly removed with a reaction at high temperature with metallic magnesium.

In the joint paper of January 1895, Rayleigh told the story of his progress

towards a quantitative and quick preparation of pure argon. He started the experiments with an apparatus in which the reaction vessel was simply a test-tube. In a note added in the following April, Rayleigh remarked: "The apparatus [...] has proved to be convenient for the purification of small quantities of argon, and for the determination of the amount of argon present in various samples of gases, e.g., in the gases expelled from solution in water" [38]. Obviously, the apparatus was not suitable for a quantitative preparation: "The principal objection to the oxygen method, as hitherto described, is the extreme slowness of the operation". Thus, he changed design and dimensions, and later in the paper describes a "plant with which the large scale operations have been made". However, Rayleigh admits that "[t]he apparatus has been varied greatly, and it cannot be regarded as having yet assumed a final form". In this precarious practical situation, the tenacious physicist falls back at first on the description of a preliminary "experiment in which a tolerably good account was kept of the air and oxygen employed", and after the analysis of several experimental difficulties he depicts "[t]he most convenient apparatus for large-scale operations that has hitherto been tried". In this case the reaction run in "a large globe of about 6 litres capacity", but Rayleigh was yet unsatisfied. When the paper was in print, he added a new page, dated again April 1895. Now, "the capacity of the working vessel is 20 litres", and "the apparatus has been kept in operation for fourteen hours continuously, and there should be no difficulty in working day and night" [38].

In the same month of April 1895, Rayleigh gave a lecture at the Royal Institution, in which again he describes the several apparatuses, and – as the only speaker – he has to treat also the competing preparation: "I must pass on the alternative method which has been very successful in Professor Ramsay's hands" [64]. After a short description of Ramsay's method, Rayleigh admits his doubts:

"I should have liked at this point to be able to give advice to which of the two methods – the oxygen method or the magnesium method – is the easier and the more to be recommended; but I confess to be quire at a loss to do so".

At last, he seems to suggest a disciplinary difference:

"If the alternate currents are at hand, I think it may be possibly the case that the oxygen method is the easier; but, otherwise, the magnesium method would, probably, be preferred, especially by chemists who are familiar with operations conducted in red-hot tubes" [64].

Actually, in 1895 for Rayleigh the most urgent problem was to obtain a quantity of argon, which was sufficient for a 'personal' density measure; the value proposed in the joint paper (19.941, $O_2=16$) had been determined by Ramsay. It was only in January 1896 that Rayleigh published his result (19.940, $O_2=16$), measured on gas prepared with the 6 litres apparatus [65]. Anyway, Rayleigh was not yet satisfied of his apparatuses, and in 1897 he published on the *Journal of the Chemical Society* an article which described his numerous attempts of bettering the yield of argon with apparatuses working at a high pressure, and which ended with the description of the 'final' preparative apparatus: in this case the working vessel was of 50 litres [66].

In downright contrast to his competitive 'chemical' attitude, Rayleigh did not participate to the determination of the argon monoatomicity through the measurement of the sound speed in the new gas. The determination that the molecule of argon was monoatomic was entirely based on the kinetic theory of gases and on the equipartition of energy, via the well-designed experimental method of August Kundt, based on the measurement of sound speed. A formula let calculate the ratio γ of specific heats at constant pressure and volume, and the theoretical ratio $\gamma = 1.67$ for monoatomic gases was confirmed by Kundt and Emil Warburg with measurements on mercury vapour. In Ramsay's hands, the experimental method became extremely elegant [49], and gave a sharp result: "the ratio of the specific heats is practically 1.66:1" [38]. However, the several reported measurements on diatomic gases gave results much less convincing, and - overall - the same fundaments of the kinetic theory of gases seemed feeble and arbitrary to many researchers. In 1900, Rayleigh's judgment on the equipartition of energy was drastic: "for some reason not yet explained the doctrine fails in general" [69]. Rayleigh was concerned about the ambiguous epistemic status of the equipartition of energy and of its consequences on the ratio of specific heats, and this condition of uncertainty could be the reason why he - a major expert of sound phenomena and theory - never tried to measure the sound speed of argon and of the other gases of interest.

In the biography of the father, Robert Strutt reports that, during the scientific turmoil due to the discovery of argon, Rayleigh said: "I want to get back from Chemistry to Physics as soon as I can. The second-rate men seem to know their place so much better" [73]. As matter of fact, Rayleigh still worked in preparatory chemistry for many years. It is a pity that he knew only one of the more boring and difficult – albeit fundamental – side of chemistry.

SIR JOSEPH JOHN THOMSON: AN INSIDER

The first approach to chemistry by Joseph John Thomson (1856-1940) was precocious. In 1882 Thomson win the Adams Prize with a long physical mathematical essay on Helmholtz' vortexes, and in 1883 he published an enlarged version under the title *A Treatise on the Motion of Vortex Rings*. In the few lines of the preface he wrote: "I have not made any alterations in the first three parts of the essay: but to the fourth part, which treats of *a vortex atom theory of chemical action*, I have made some additions in the hope of making the theory more complete" [75]. The ambitions of the young physicist are restated in other two points of the introductory pages: "a sketch of a vortex atom theory of chemical action", "a sketch of a vortex theory of chemical combination". The additions to the original text are in the last paragraphs of the essay: in §58 ("Sketch of a chemical theory"),

\$59 ("Theory of quantivalence"), and \$60 ("Valency of the various elements"); this last paragraph was completely new. As regards the epistemic approach, Thomson is fully Maxwellian when states: "the vortex ring obviously possesses many of the qualities essential to a molecule that has to be the basis of a dynamical theory of gases. It is indestructible and indivisible". After more than one hundred pages of calculations, Thomson describes his atomic-molecular model:

"[T]he atoms of the different chemical elements are made up of vortex rings all of the same strength, but [...] some of these elements consist of only one of these rings, other of two of the rings linked together, [...] and so on. [...] Thus an atom of an element may combine with another atom of the same kind to form a molecule of the substance consisting of two atoms" [75].

The last sentence of the passage gives the best (if not the only) result of the long mathematical tour de force, the stability of a diatomic elemental molecule. Many other 'results' have no chemical consistency at all, the most stupefying 'result' being the bivalence of carbon.

From the existence of CO, Thomson deduces that in *all* compounds the carbon atoms are bivalent, and writes: "the molecules of carbonic acid and marsh gas have each three primaries represented by C-O-O and C-H₂-H₂ respectively" [75]. These molecular models ignore not only the theory of valence (27 years old for the tetravalent carbon), but also the stereochemistry of carbon compounds (nine years old); for any chemist it was unacceptable a molecular model as C-H₂-H₂, with three 'entities' at the vertices of an equilateral triangle. Thomson goes on explaining "the carbon atom must have only twice as many links as the hydrogen atom", and he is really pleased with himself:

"[T]his view is supported by the composition of acetylene C_2H_2 ; if the valency of carbon be two, the molecule may be divided into the three primaries C-C-H₂, but if the valency of carbon were four, the molecules of acetylene could not be divided into primaries of equal strength, so that according to our view, its constitution is impossible on this supposition" [75].

Thomson's second significant appointment with chemistry was in 1893, in the first pages of the *Notes on Electricity and Magnetism*. Here we find the heuristic use of the Faraday tubes, that he presents as "real physical quantities having definite sizes and shapes". In this context, he also presents a model of chemical bond:

"When the length of the tube connecting two atoms is comparable with the distance between the atom in a molecule, the atoms are said to be in chemical combination; when the tube connecting the atoms is very much longer than this, the atoms are said to be 'chemically free'" [76].

Actually, Thomson wishes to propose "a kind of molecular theory of electricity, the Faraday tubes taking the place of the molecules in the Kinetic Theory of Gases", and still ads: "These tubes also resemble the molecules of a gas in another respect, as we regard them as incapable of destruction or creation" [76]. After the measurement of the value of e/m – the 'discovery' of the electron – in 1897, and several years of reflections, Thomson published a capturing article "On the Structure of the Atom" [77]. Among the many important results, the Author underlines his physical mathematical explanation of the periodic system of the elements. The point is crucial and at length expounded in the paper; the argument sounds persuasive, however an attentive reader could find a contradiction. The model relationship between the members of a group of elements is presented in this passage:

"We regard a series of atoms formed in this way, *i.e.* when the atom of the *p*th member is formed from that of that of the (*p*-1)th by the addition of a single ring of corpuscles, as belonging to elements in the same group in the arrangement of the elements according to the periodic law; *i.e.* they form a series which, if arranged according to Mendeléef's table, would all be in the same vertical column" [77].

Thomson discusses in many details the series of nine stable systems of 59-67 corpuscles, each with 20 corpuscles in the outer ring, and concludes:

"[W]e have at the beginning and the end systems which behaves like atoms of an element whose atom are incapable of retaining a charge of either positive or negative electricity".

"Thus we have the series of elements:

]	He	Li	Be	В	С	Ν	Ο	F	Ne
]	Ne	Na	Mg	Al	Si	Р	S	Cl	Arg.
The fi	rst and	last ele	ment in	each o	f these	series h	as no va	lency"	[77].

The contradiction is evident. In the later quotations Thomson affirms that two systems with *equal* number of corpuscles in the outer ring belong to the same group of noble gases, while according to the former quotation the two systems should have a *different* number of corpuscles (20 vs. 21, in the proposed example).

As far as I know, the contradiction went unnoticed, and this it is – in a sense – obvious, because the model was acceptable and was accepted by chemists, in that it explained the different electronegative and electropositive behaviour of the elements and the ionic kind of chemical bond.

Thomson and chemistry: follow up

The two atomic models of 1883 and 1904 are separated not only by two decades of scientific progress, but also by a deeper understanding of the chemists' way of reasoning. In the following two decades, while for several reasons Thomson's scientific activity went away from the main stream of theoretical physics, his contributions to chemical theories became increasingly interesting – at least for chemists.

Thomson's 'chemical' proposals were complex and structured, and they found an attentive audience in the United States. In May 1903, Thomson gave at Yale the Silliman Lectures, whose text was published the following year under the evocative title *Electricity and Matter* [78]. A second noteworthy effort of high popularisation (and working-out) was the series of lectures given at the Royal Institution in the spring of 1906. The lectures were printed as *The Corpuscular Theory of Matter* in 1907 [79]. The Silliman lectures and the two books had a definite impact on the American chemical community [58].

A crucial year for Thomson and for our story was 1913. For Thomson this year was a year of difficulties. On the ups side we find that on 22 May Thomson held the Bakerian Lecture at the Royal Society; on 11 September, at the Birmingham meeting of the BAAS in a special session, he presented his last atomic model to an excellent audience, which included Rutherford, Jeans, Curie, Lorentz, and Bohr; on 4 October he sent to the press a remarkable book with a title which made clear his new scientific interest: Rays of Positive Electricity and Their Application to Chemical Analysis [80]. Only one event was on the downs side, but unfortunately for Thomson, it was the most important. In November 1912, Thomson had been invited by Hendrik Lorentz to give the first report on the atomic structure at the next Solvay Conference [23], to be held in Brussels in the October of the following year. Actually, the Conference began on 27 October 1913, with Thomson's report on the structure of the atom; the report was unsuccessful, almost disastrous. Rutherford was respectfully prudent; Nernst, Langevin and Rubens expressed their perplexity, but the objections by Curie and Lorentz were radical - Lorentz doubted that Thomson's model was coherent also in the frame of the classical mathematical physics [46]. The model was based on a couple of radial forces, attractive and repulsive [81], and it had in the chemical community a 'success' not better than that obtained in the physical community.

Thomson always preferred the *Philosophical Magazine* for his scientific contribution, also after 1913, when his articles became increasingly interesting for the chemical community. In May 1914, the journal of British physicists opened the fascicle with a long article by Thomson, on a molecular-chemical theme "The Forces between Atoms and Chemical Affinity". The epistemological evaluation on the atomic theory is stated by the Author in the first page:

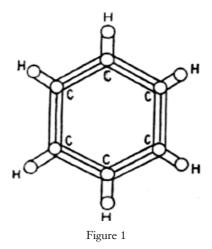
"The consideration of the mutual action between atoms is perhaps the most important part of the atomic theory, for on it depends the explanation of the majority of chemical as well as of physical phenomena" [82].

The article presents many points of great interest for the chemical theory, and I analysed them elsewhere [9], here I mention only two of his most important proposals. The third and last part of the paper is dedicated to "the conditions for the existence of a Chemical Compounds and on Valency" [82]. In this context, the Author specifies the features of his atomic model in function of its chemical behaviour:

"There may be a ring of corpuscles near the surface of the atom which are mobile and which have to be fixed if the atom is to be saturated. We suppose, moreover, that the number of corpuscles of this kind may be anything from 0 to 8, but that when the number reaches 8 the ring is so stable that the corpuscles are no longer mobile and the atom is so to speak self-saturated.

The number of these mobile corpuscles in an atom of an element is equal to the number of the group in which the element is placed on Mendeleef's arrangement" [82].

It is seen here that Thomson is now sparing of corpuscles, and that his position on the electronic atomic structure is very similar to that proposed by Abegg in 1904 (Abegg is quoted by Thomson [82]). My second remark is on the proposed electronic structures of benzene (See Figure 1) and naphthalene. With these proposals, Thomson entered the *sancta sanctorum* of organic chemistry, and without any doubt, they were accepted as an important suggestion by the most attentive members of the chemical community [10].



Certainly very attentive was Gilbert Newton Lewis, who in his classical article of 1916 establishes the modern conception of chemical bond, and refers to Thomson's paper five times [31].

In the article of 1914, Thomson displays a good chemical culture, which is surely the result of study and reflection. After the tragic interval of the Great War, Thomson develops his research essentially in theoretical chemical fields. In 1921, he published a long article on the molecular structure, in which cubical, static atoms appear, but without any emphasis ("to simplify the diagram the cells are represented as cubes" [83]). The reference to Lewis is cursory, however Thomson epistemic debt is clear, because only now he is persuaded of the essential trait of the chemical bond, proposed by Lewis in 1916: "Inasmuch as each bond of this kind requires two electrons, the symbol, whether a line or a dot, used by chemists to denote such a bond represents two electrons" [83]. Here, it is fair to quote what Lewis wrote in 1916: "It is evident that the type of union which we have so far pictured, although it involves two electrons held in common by two atoms, nevertheless corresponds to the single bond as it is commonly used in graphical formulae" [31].

The last year that is of interest for us is 1923. In this year, Thomson lived a full immersion in chemistry. In April, he held a series of lectures at the Franklin Institute of Philadelphia; in the following June, he delivered the manuscript of the lectures to Chapman & Hall, and the text was published under the title *The Electron in Chemistry* [84]. In the preface, Thomson feels the necessity of justifying the thematic choice: "The choice of chemistry as a subject for lectures by one whose work has been mainly in physics seems to call for some explanation". However, the explanation is simple:

"From many points of view the chemical side seems to be the one on which the most striking developments of the newer physics may be expected. In the first place the problems are of the greatest intrinsic importance and, secondly, in the vast mass of information accumulated by chemists with regard to the combination of atoms we have *unrivalled means of testing the truth* of any conclusion to which the theory may lead us" [84].

My italics underline the phrase in which Thomson pays chemists epistemological compliments that are very rare from a great physicist. On the other hand, the community of chemists returned the admiration, an admiration that was realized in a very meaningful, social-scientific event in July 1923. In 1920 Thomas Martin Lowry has became the first professor of Physical Chemistry in Cambridge. Three years later, in occasion of the 25th anniversary of the discovery of the electron Lowry organized in Cambridge a meeting of the Faraday Society on the electronic theory of valency. Thomson was the chairman of the General Discussion, and the introductory lecture was given by G.N. Lewis. Other two general lectures were given by the physicist R.H. Fowler and by the chemist N.V. Sidgwick; communications were given by Lowry, Lapworth, and Robinson [10]. The 'chemical year' of Thomson was completed by the publication of an important article in which he discussed one of the most popular themes of organic chemistry [85].

We followed the journey of Thomson towards and through chemistry for forty years, since 1883 until 1923, a very long period in a scientific life and in the life of science. Thomson's entry in the 'wild variety' of chemical theoretical 'objects' was not easy, however since 1904 his contributions were increasingly important, and – as we saw – after the defeat at the second Solvay Conference his principal scientific interlocutors were the chemists. In my opinion, it is no accident that Thomson began the academic career just when Kelvin was changing his mind about chemistry, and Rayleigh was thinking to challenge the chemists on the reserved field of the atomic weights determination. Thomson felt keenly the heuristic power of the chemical theories, a feeling very different from that of his younger colleague, Ernest Rutherford.

ERNEST RUTHERFORD, FIRST BARON RUTHERFORD OF NELSON: THE PARADOX

The collaboration between Ernest Rutherford (1871-1937) and Frederick Soddy (1877-1956) at McGill University of Montreal is one of the most famous in the history of science, because it is beyond comparison for its scientific results and – probably – for its shortness. Their collaboration lasted for one year and half, from mid-October 1901 until mid-April 1903; in eighteen months they jointly authored nine papers. During nine years at McGill, Rutherford published 69 papers, either alone or with a second author, with several excellent results (as the determination of the sign of the alpha-particles charge); in this period he worked with ten different researchers, including Soddy and Otto Hahn. In the context of Rutherford's creativity and collaborative style of work, the collaboration with Soddy was not particular, while very particular were the circumstances of their encounter.

Rutherford & Soddy

Soddy was twenty-two years old when he applied for a Chair of Chemistry in Toronto. Uninvited, he went in 1900 from Oxford to Toronto, only to apprehend that the chair had been given to a local incumbent. He was advised to go to Montreal, where new chemical laboratories had been just opened, and perhaps new staff was needed. At McGill Soddy accepted the initial position as demonstrator. Since the beginning of his studies, Soddy was interested in the problems at the border of chemistry with physics; in a juvenile essay, he wrote: "The vast field of research [...] between chemistry and physics is almost virgin" [92]. On the contrary, Rutherford's genius was completely dedicated to the art and mysteries of physics; it is reported that when he was in Manchester he quipped: "All science is either physics or stamp collecting" [1]. Even now, this quotation is very popular, as it is another one by Dirac, which we will find later; Rutherford's sentence rests only on ideological ground, and as such, it is used without shyness.1 At McGill the New Zealander physicist had held a similar opinion, on the unquestionable superiority of physics on the other disciplines, as it is demonstrated by his attitude before the first encounter with Soddy.

In December 1900, Soddy was asked to participate in a discussion at the McGill Physical Society, on themes of common interest and with Rutherford as antagonist. The debate was scheduled at the Society meeting towards the end of March 1901. At the eve of the discussion Rutherford wrote to Thomson:

¹ In 2004 B. Hayes wrote: "A century later, surveying the state of physics and its relations with other fields, I am tempted to give Rutherford's quip an even more inflammatory reading, though he never intended it. «All science is physics» might be taken as a territorial claim, annexing other disciplines as provinces to be ruled by the laws of physics and administered by physicists. This imperial vision of the destiny of physics is not entirely without a basis in history, or at least etymology" [25].

"Corpuscular theory seems to take the field in Physics at present [...] We are having a great discussion on the subject tomorrow in our local 'Physical Society' when we hope to demolish the Chemists" [92].

The debate was about fundamental issues as the electrical nature of the electron 'mass' and (probably) of every mass. An outcome of the debate was that the physicist's atoms were not the chemical atoms, which Soddy thought endowed with "concrete and permanent identities, if not immutable, certainly not yet transmuted" [92]. On the personal ground, the discussion generated a sense of mutual respect in the two young researchers.

It was in summer 1901 that Rutherford convinced himself that it was important to ascertain the chemical nature of thorium emanation [radon]. He asked his senior chemical colleague for collaboration, but had to fall back on a junior aid – namely Soddy, who accepted at once. Their actual collaboration began in laboratory on 12 October, and their first paper was send to London for publication on the *Journal of the Chemical Society* just before Christmas.

Among the nine joint papers, at least five are very important: the first four and the last one. The first two were published respectively in April [50] and in July [51] 1902 on the *Journal of the Chemical Society*, the third and the fourth were published on the *Philosophical Magazine*, respectively in September [52] and November [53]. The detailed textual history of these four articles could disclose many aspects of the knowledge procedures of the two Authors, but here we may be satisfied by a couple of remarks.

The choice of a chemical journal for announcing the discovery of the transmutation of elements gives us several clues to the meaning that the Authors gave to their spectacular results. The two 'chemical' papers have a common title: "The Radioactivity of Thorium Compounds", and different sub-titles; one is 'chemical', in that it refers to a substance: "An Investigation of the Radioactive Emanation", the other is definitely more ambitious and 'physical': "The Cause and Nature of Radioactivity". In the first instalment of 30 pages Rutherford and Soddy gave many experimental, chemical and physical data, and they conclude that: "the emanation is a chemically inert gas analogous in nature to the members of the argon family" [50]. However, they were still uncertain on the mechanism of the radioactivity connected with the generation of emanation: "[emanation] might conceivably be an inert gas continuously emitted in the radioactive state" [50]. A central point of the paper regards the instrumental side of the investigation; in a section titled "The Chemical Aspect of the Question", the Authors extol the power of the electrometer method of measuring, which can detect "a quantity of the order of 10-12 that detected by the balance" [50]. The conclusion that the succession of radioactive processes is accompanied by an extraordinary phenomenon is reached only in the second 'chemical' paper, and it is announced without any particular emphasis: "radioactivity is at once an atomic phenomenon and the accompaniment of a chemical change in which new kind of matter are produced" [51]. The last words of the paper are: "it is not unreasonable to hope that radioactivity affords the means of obtaining information of processes occurring within the chemical atom" [51].

The articles published on the *Philosophical Magazine* were more the consequence of a long theoretical reflection than of the outcome of new experimental results (*vide infra*). This important fact is shown in Scheme 1.

	Sc			
		Ch 1.1	\rightarrow	Ph 2.1
Ph 1.1	←	Ch 1.2		
Ph 1.2	←	Ch 2.1		
Ph 1.3	←	Ch 2.2		
		Ch 2.3	\rightarrow	Ph 2.2
Ph 1.4	←	Ch 2.4		
Ph 1.5	←	Ch 2.5		

Ch 1.*n*, *Ch* 2.*n* are the figures of the 'chemical papers'; *Ph* 1.*n*, *Ph* 2.*n* are the figures of the 'physical papers'.

The 'chemical' paper presents seven figures; the two in the first paper describe experimental apparatuses; the five in the second paper are diagrams describing the recovery and decay of the radioactivity in different experimental sets. Following the Scheme 1, we see that the two 'physical' papers are rhetorically a reshuffle of the two 'chemical' papers. Now Rutherford and Soddy are more sure about the atomic mechanism of radioactivity, and the sub-title of the second 'chemical' paper became the general title of the two 'physical' papers: "The Cause and Nature of Radioactivity". From the theoretical point of view the first 'physical' article does not add nothing of really new, while in the second article, in the last section, the Authors shift the radioactivity from the daughter substance (thought in a "radioactive state") to the parent substance: "Radioactivity may be an *accompaniment* of the change, the amount of the former at any instant being proportional to the amount of the latter" [53, italics in the text]. In our context, the most important point is that the same experimental basis suited equally well two different, innovative discourse addressed respectively to chemists and to physicists.

A 'chemical change'?

Rutherford was aware of running for the Nobel Prize, however he was greatly surprised at the assignment of the prize for chemistry [26]. The reasons and the cir-

cumstances of the assignment of the Nobel Prize are very specific for every single prize, and the Rutherford case is no exception. However, we are not interested in the twisted path, which led to Rutherford's prize, but in an understanding of the conception shared by Rutherford and Soddy, that radioactivity was a 'chemical change'. In fact, our researchers had to face a fundamental linguistic and epistemological choice about the nature of the production of "new types of matter": was it a chemical or a physical phenomenon? To be sure, the problem was not completely new. In 1899, the two German physicists Julius Elster and Hans Geitel wrote:

"The property of emitting Becquerel rays [...] cannot really be interpreted as a manifestation of a chemical process in the usual sense. On the contrary, the source of energy must be sought in the atoms of these particular elements" [22].

Elster and Geitel introduced their interpretation with a very clear *on the contrary*, a phrase which counter the usual, chemical, molecular process with a yet unknown atomic, physical process. At this point, the two German physicists used a chemical model for explaining the physical phenomenon:

"A radioactive element consists of atoms, similar to the molecules of an unstable chemical compound, capable of undergoing a transformation to a stable state with the release of energy. If this be the case then the active substance must gradually become transformed into an inactive one with a corresponding modification of its properties as a chemical element" [22].

Rutherford and Soddy too thought that radioactivity was not a 'usual' chemical process, but in 1902 they did not have yet a clear image of the process. As we saw above, in the second 'chemical' paper they wrote, "radioactivity is at once an atomic phenomenon and the accompaniment of a chemical change in which new kind of matter are produced" [51]. This phrase was maintained in text published *ad usum physicorum* [52], but the following passage in the 'chemical' paper was deleted in the 'physical' paper:

"The idea that the chemical atom in certain cases spontaneously *breaking up* with evolution of energy is not of itself contrary to anything that is known of the properties of atoms, for the causes that bring about the *disruption* are not among those that are yet under our control, whereas the universally accepted idea of the stability of the chemical atom is based solely on the knowledge we possess of the forces at our disposal" [51, added italics].

In my opinion, Rutherford and Soddy spoke of a 'chemical change' for two reasons. The first reason is merely semantic: the change was defined 'chemical' because it changed the *chemical properties* of the substances. The second reason was epistemic and epistemological, with chemistry offering a first interpretation of the process (the epistemic side) and consequently dominant in the science hierarchy (the epistemological side). The usual, chemical reaction was *the* model. In the first 'chemical' paper they gave this definition: "the emanating power or *rate* at which the emanation is produced per unit weight of substance", and stated: "the property appear [...] as the result of a dynamical change, possibly in the nature of a chemical reaction" [50]. In the second 'chemical' paper and in the first 'physical' paper they use strictly disciplinary terms: "the change [...] is of the type of a decomposition rather than depolymerisation" [51]. Eventually, at the end of the second 'physical' paper the Authors recall the equation which gives the curve of decay of ThX [52] and state:

"The law of decay of the activity with time (equation 1, first part) [...] appears as the expression of the simple law of chemical change, in which one substance only alters at a rate proportional to the amount remaining" [53].

The law for a reaction of first order was a 'chemical law', as well as all the reactions known then were the chemical reactions, studied in the chemical laboratories. On this basis, it is not surprising that also the radioactivity, which followed the same law, was understood as a 'chemical change'.

Obviously, the 'change' issue was still open for the Authors and for their readers, as it is shown in the German translations of the 'physical' papers. On 11 June 1902, Rutherford and Soddy send the manuscripts of their two articles to the Editors of the *Zeitschrift für Physikalische Chemie* with an accompanying letter in which they wrote:

"[The papers] contain an account of work which has already been forwarded to the London Chemical Society during the progress of the investigation. The results have been rewritten in logical sequence in the present papers from the point of view of the advances made" [92].

The papers were published respectively in October [54] and in December [55] 1902, and were translated by Wilhelm Böttger, a 'ionist', colleague of Wilhelm Ostwald. As a translator, Böttger had to be a very attentive reader. At a glance, it is seen that the translation was somewhat faithful; so two 'deviations' from this faithfulness are interesting for us. The German 'ionist' found that in that particular context the words lchemical changel could have at least three different translations, with lchangel translated as: lUmsetzungl (5 occurrences), lVorgangl (2 occurrences) and lVeränderungl (3 occurrences). The semantic difficulty of the reader/translator is evident; it clearly reflects the novelty of the knowledge situation. Passing from the reader/translator to the Authors, we find that in a crucial passage they put in the manuscript a new, enlightening phrase. In the first 'physical' paper we read:

"Radioactivity may therefore be considered as a manifestation of subatomic chemical change" [52].

In the German translation, we find this text:

"Die Radioactivität kann daher als eine Äusserung von chemischer Verändrung von Teilchen angesehen werden, die unterhalb der Grenze der Atome stehen" [54].

The phrase subatomic chemical change is 'explained' with a new phrase, something as "chemical change of particles which are below the boundary of the atoms". Eight years later, after a long reflection, Rutherford accepted the verdict of the experimental data and proposed the nuclear model of the atom. At last, he was penetrating 'below the boundary'.

PAUL ADRIEN MAURICE DIRAC: THE PUREST SOUL

There are many reasons for concluding our research with a mention of P.A.M. Dirac (1902-1984), but I restrain myself to only three.

Dirac was one of the founders of quantum mechanics, the only one not of German or Hungarian origin. Since quantum mechanics is an alleged competitor of experimental chemistry, it may be epistemologically useful to look at one of its founders.

In 1929, Dirac published a paper on the "Quantum Mechanics of Many Electrons Systems"; albeit important in itself, this article owes great part of its fame to Dirac's *incipit*, which since then is a central issue in the permanent debate on the reduction of chemistry to physics. In the present research too, that *incipit* will focus our attention.

The last reason is that it seemed to me meaningful (and delightful) to close my narrative with a reference to a supreme scientist, who had a scientific and personal stature comparable to that of Maxwell. Of course, 'comparable' does not mean 'similar'. For example, Dirac was fundamentally atheist, while Maxwell was fundamentally theist; however Maxwell too could fall under Bohr's opinion of Dirac ("Of all physicists, Dirac has the purest soul" [48]).

Before reading and commenting Dirac's famous passage, let us put it in the intellectual context in which it was written. Dirac send the article on the manyelectron systems to the Royal Society in March 1929 (through R.H. Fowler) and it was published on the *Proceedings* in April 1929. Since the beginning of this year the young theoretical physicist was writing his fundamental book, The Principles of *Quantum Mechanics*; the book appeared in 1930, and the first edition was sold out quickly [15]. Through revisions and expansions, the book had four editions and one reprint during Dirac's life. In the first paragraph of the book, Dirac states: "quantum mechanics [...] has now reached a form in which it can be based on general laws and is, although not yet quite complete, even more elegant and pleasing than the classical theory in those problems with which it deals" [18]. The Author's epistemic and ontological position is given just at the end of the paragraph: "The waves and particles should be regarded as two abstractions which are useful for describing the same physical reality. One must not picture this reality as containing both the waves and particles together [...]. What quantum mechanics does is to try to formulate the underlying laws in such a way that one can determinate from them without ambiguity what will happen under any given experimental conditions" [18]. These two quotations contains several key words (here with added italics) that we will find again in the famous *incipit*:

"The general theory of quantum mechanics is now almost complete, the imperfection that still remain being in connection with the exact fitting in of the theory with relativistic ideas. These give rise to difficulties only when high speed particles are involved, and are therefore of no importance in the consideration of atomic and molecular structure and ordinary chemical reactions in which it is, indeed, usually sufficiently accurate if one neglects relativity variation of mass with velocity and assumes only Coulomb forces between the various electrons and atomic nuclei. The *underlying physical laws* necessary for the mathematical theory of a large part of physics and the whole of chemistry are thus completely known, and the difficulty is only that the exact application of these laws leads to equations much too complicated to be soluble" [17].

The connections between the two texts are evident:

The article: general theory almost complete The book: general laws not yet quite complete The article: underlying physical laws The book: underlying laws

In other words, the *incipit* was written in the same intellectual, exciting context of the book. At the end of 1920s, Dirac viewed the situation in physics optimistically, and on some occasions came close to the idea that physics was in principle complete; then, this view was fashionable among quantum physicists, furthered by the amazing success of the 1928 wave equation of the electron [30]. In this context, chemistry offered Dirac no insuperable obstacle, because, along with our Author, "molecular structure and ordinary chemical reactions" escaped the difficulties tied to relativistic effects. Dirac's statement that "the mathematical theory of a large part of physics and the whole of chemistry" had a reliable physical base was not a rash judgment, but the inescapable conclusion of a reflection on the *whole* of quantum mechanics. However, the following history of chemistry and physics did not meet Dirac's optimistic expectations. The failure of the annexation of chemistry by quantum mechanics is not due to "to equations much too complicated to be soluble", but because "[n]either the topology nor the ontology appropriate to molecular structure can be derived from or found in quantum mechanics alone. Hence, an empirically and explanatorily important structure in molecular chemistry looks to be missing from quantum mechanics" [2, see also 16].

Dirac's position has been quoted such many times, and by important Authors, that the chemists' citations have been studied from an historical point of view [56]. Obviously, also physicists' citations are of similar interest; for example that by John H. van Vleck in his Nobel Lecture of 1977: "To stress the importance of the quantum mechanical revolution, I cannot do better than to quote an often-mentioned sentence from one of Dirac's early papers" [93]. Physicists' citations are of interest partly because the problem of reductionism is not solved at all, if two very competent historians of science can write: "The community of physicists, in any case, came under the spell of Dirac's reductionist program, expressed as a theoretically correct, but practically meaningless dictum" [24]. I do not think that Dirac's epistemic position is "theoretically correct" (*vide supra*).

A last remark regards the failure of another aspect – strictly epistemic – of Dirac's thought. In the first edition of the *Principles* Dirac laid down a precise commandment: "One must not picture this [atomic] reality" [18]. In the second edition, Dirac tried to explain himself; when he discusses the questions of superposition and indeterminacy he gave a cryptic 'explanation' of what is a 'picture' of the atomic world:

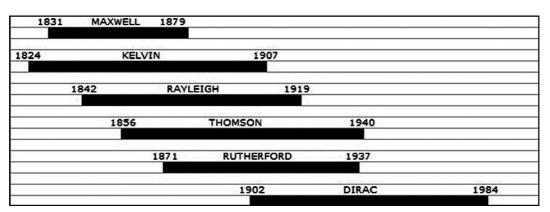
"In the case of atomic phenomena no picture can be expected to exist in the usual sense of the word 'picture', by which is meant a model functioning essentially on classical lines. One may extend the meaning of the word 'picture' to include any way of looking at the fundamental laws which makes their self-consistency obvious. With this extension, one may acquire a picture of atomic phenomena by becoming familiar with the laws of the quantum theory"[19].

In spite of (or because of) this explanation, Dirac's commandment was ignored both in physics and in chemistry. In any case, it was not possible for chemists to give up that fundamental part of their knowledge procedures which is based on paper tools [29].

Conclusions: the parabolic curve

An important issue is at halfway between philosophy of science and ideology: it is the perception shared by almost all the physicists that the world, in any minute particular, obeys to general laws. This attitude towards the epistemological value of the scientific results leads without any mediation to the establishment of hierarchies, and it is from this point of view that we can better understand the above quoted sentences by Rutherford and Dirac. Rutherford thought that only physics was able to discover general laws, and Dirac was sure that the most general law of nature had been eventually discovered. Both scientists missed two fundamental epistemic traits of chemistry. The first epistemic trait is that there are no general 'chemical' law, because any substance has a particular behaviour also in the simplest reaction; any substance is a chemical individual [94]. Chemistry and biology shares the crucial issue of the individual, irreducible behaviour of their research 'objects', e.g. substances or species. Thus, chemistry is not the only great scientific discipline to defy the physicists' ideal of few general laws, able to explain all the multifarious phenomena of the real world; nevertheless, as a matter of fact, many chemists share the dream of Rutherford and Dirac.

The second epistemic trait missed by Rutherford and Dirac is the constructive ability of chemistry; as Berthelot said in 1860: "La Chimie crée son objet, cette faculté créatrice semblable à celle de l'art lui-même, la distingue essentiellement des sciences naturelles et historiques". This essential trait was perfectly understood by Kelvin and Thomson, but completely ignored by the other four physicists here discussed. The case of Maxwell is particularly meaningful, because of his lasting faith in the immutability of molecules while he was living in the exciting period of the developing synthetic abilities of chemists. Without any doubt, the social prestige of chemistry declined in the last part of the Twentieth Century [12]. Perhaps, the highest point of the prestige parable was reached in the two decades after the end of the Second World War, when everywhere in the industrialised world enormous investments shifted the chemical industry from coal to oil as feedstock. As regards the British physicists, the parable of the academic interest reached its maximum long before, probably just before the First World War.



Scheme 2

We can look at the Scheme 2, where the lifespan of our six physicists is reported. In the years around 1900, four physicists were active: Kelvin, Rayleigh, Thomson and Rutherford; through very different routes, all of them were or became deeply interested in chemical affairs. In the second decade of the century, two new research fields opened before the most advanced physicists: the nuclear physics, inaugurated by Rutherford, and the atomic-molecular quantum physics, inaugurated by Bohr. Rutherford, the Nobel Prize in chemistry, went along his way, very far from chemistry. Thomson, the Nobel Prize for the discovery of the electron, was considered 'retired' by the physical community. Dirac, the Nobel Prize for his contribution to quantum mechanics, claimed with angelic impudence that "the mathematical theory of the whole of chemistry" was handy. In the 1930s, at Cambridge the interests of the mainstream physicists were far from the fundamental chemical problems, as the relationship between the molecular electronic structure and reactivity. This kind of problems became the field of research of other physicists and chemists who founded a new strange sub-discipline – quantum chemistry.

Probably, six points (or lives) are not enough for tracing a dependable historiographical course, however the analysis of the six different attitudes towards chemistry evidences several historical and philosophical aspects of the relationship we are discussing. The first aspect is that the disciplinary relationship between physics

and chemistry changed deeply in time, with a succession of our scientific leaders'

indifference \rightarrow interest \rightarrow indifference

attitude akin to the following one:

The indubitable, historical fact of a mobile awareness questions a large part of the work of the traditional philosophers of science, who try to find stable ontological hierarchies in the real world as well in the scientific world. Not only in my opinion, the alleged ontological hierarchies are imaginary, and used as a justification of academic and social hierarchies [20-21].

The time lag between the maximum of physicists' interest and the maximum of social-economic role of chemistry seems to demonstrate a fair independence of the epistemological perception of disciplines from the general economic situation. This aspect is understandable. Of course, the perception of the disciplinary hierarchies arises from several sources, academic as well social, and it is heavily conditioned by a deep, but sometime unnoticed, feeling of identity with the discipline. All our physicists felt this feeling; nevertheless, their epistemological situation was different. Among the several components of a personal scientific attitude, it is important the presence of a strong epistemic/epistemological interest, because this kind of interest leads to a tight control of the knowledge procedures (the epistemic side) and to a more or less liberal check into the hierarchies inside the single disciplines and among the different disciplines (the epistemological side). Maxwell and Dirac were far in time, but near in the certainty that physics could solve any problem of the real world. For them, chemistry was of no interest. In a very different disciplinary climate, the attitude of Maxwell and Dirac was shared by Rutherford. Rutherford's epistemological indifference is important for our interpretation, because it was contemporary with Kelvin's interest as well as with Thomson's and Rayleigh involvement. The gist is that Rutherford did not perceive grave epistemic difficulties *inside* physics. Apparently, Kelvin's "Nineteenth Century clouds" [35] did not darken the disciplinary horizon of Rutherford. In various ways, Kelvin, Rayleigh and Thomson lived the crisis of the classical physics in a period in which the classical chemistry was still flourishing. In this epistemological perception we find an important source of their interest in chemical affairs.

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