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Eric Scerri

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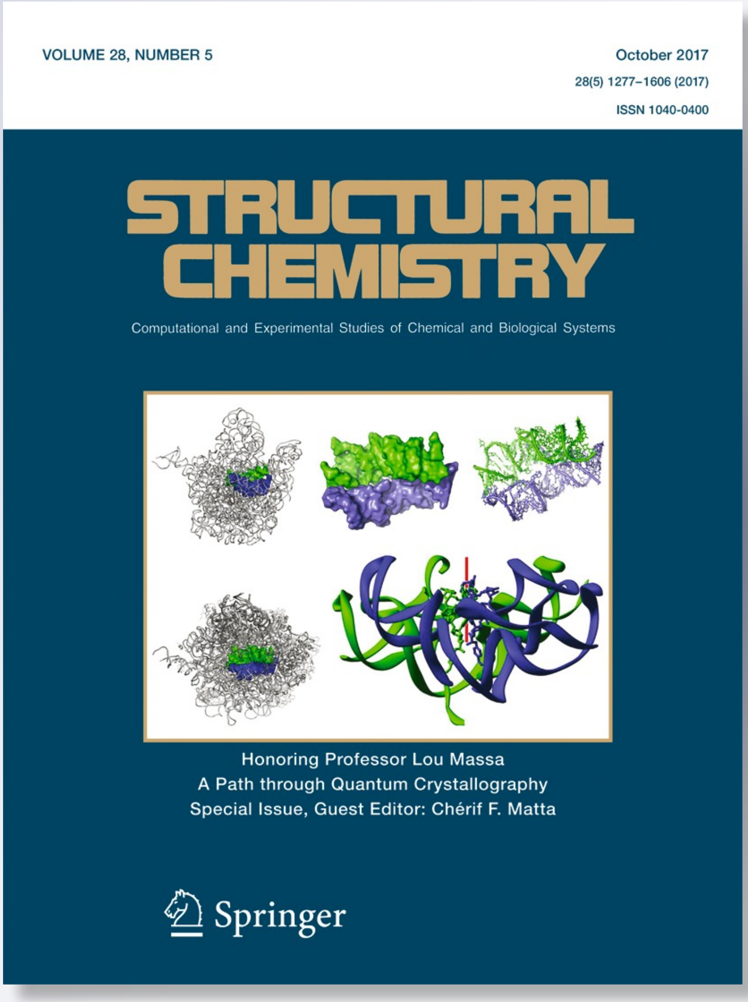

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ORIGINAL RESEARCH

The Gulf between chemistry and philosophy of chemistry, then and now

Eric Scerri[1]

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Abstract The article aims to introduce the sub-discipline of the philosophy of chemistry to the chemical community at large. The origins of the field are briefly reviewed including some possible causes for the delay in its arrival into the philosophy of science. Some critical remarks are leveled at some of the current work that has been conducted, and reasons for the gulf between philosophy of chemistry and mainstream chemistry are explored. Finally, a novel approach consists of a close examination of how scientific concepts evolve. This theme is discussed with the aid of the work of the early twentieth century amateur scientists Anton van den Broek, who first proposed that the elements in the periodic table should be ordered according to their atomic numbers rather than their atomic weights.

Keywords Philosophy of chemistry · Reduction of chemistry · Periodic table · Atomic number · Van den Broek · Rutherford · Geiger · Marsden · Evolutionary epistemology

I regret to say that I have never met Lou Massa although we have communicated in the past and I have read some of his interesting publications [1]. I was therefore delighted when Cherif Matta invited me to contribute to this Festschrift. I am also aware of Massa's interest in the philosophical aspects of chemistry, a field in which I have been working for something like 30 years. I hope that my brief article here will be of interest to Lou and to chemists in general, especially those who may be completely unfamiliar with this relatively new sub-discipline. I would also like to issue an open invitation to any chemist who might be interested in commenting on the publications that have appeared in the field, many of which have been published in the journal, *Foundations of Chemistry*.[1] I should also mention that Richard Bader and Cherif Matta were the co-authors of an article published in this journal that turned out to be Bader's last publication [2]. Moreover, Cherif edited a special issue on the work of Richard Bader to which some of the authors in this Festschrift also contributed [3]. Let me now turn to the field that I have been working in namely the philosophy of chemistry and try to explain to you what has been going on there.

Introduction & the philosophy of chemistry

Over the past 25 or so years, and unbeknownst to the vast majority of chemists, the new sub-discipline of philosophy of chemistry has been quietly developing. The field now boasts two international journals and an annual international conference, all of which have been in existence more or less since the field began to take shape,[2,3,4] In addition, there are many scholarly books and journal articles, which discuss the major themes that have been debated [4–10].

This paper is dedicated to Professor Lou Massa on the occasion of his Festschrift.

✉ Eric Scerri
scerri@chem.ucla.edu

[1] Department of Chemistry & Biochemistry, UCLA, Los Angeles, CA 90095, USA

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[1] *Foundations of Chemistry*, http://www.springer.com/philosophy/epistemology+and+philosophy+of+science/journal/10698

[2] *Foundations of Chemistry*, http://www.springer.com/philosophy/epistemology+and+philosophy+of+science/journal/10698

[3] *Hyle – International Journal for the Philosophy of Chemistry*, http://www.hyle.org/

[4] International Society for the Philosophy of Chemistry, https://sites.google.com/site/socphilchem/

Nevertheless, a wide gulf remains between mainstream chemistry and its philosophical side, even among the small number of chemists who are already aware of the existence of the philosophy of chemistry. In this article, I would like to consider the causes for the remaining gulf and to make the field better known to chemists. I would also like to offer a possible new rapprochement in the form of a novel conception of the philosophy of science, which draws its examples mainly from the borderland between chemistry and physics [11].

The very existence of the philosophy of chemistry in the current era represents something of an enigma. Philosophy of science as a whole has a considerable standing in the academic world, but it has been based almost exclusively on the sciences of physics and more recently also on biology.[5] Of course, this situation is quite understandable given that physics enjoys the role of being the most fundamental of the natural sciences and given the completely undeniable success of the reductive approach that has guided science for the past several centuries. Moreover, the philosophy of science was initially developed by philosophically minded physicists such as Percy Bridgeman, to cite just one example of many [12].

However, while the concentration on physics and the neglect of chemistry can be seen as a consequence of reductionism, it has long been clear that life itself could not be reduced to physics in the same way that chemistry was generally supposed to be reducible [13, 14]. As a result, the philosophy of biology became established something like 50 or 60 years ago in order to examine the particular themes that apply to this science. The revolution that occurred in biology with the discovery of the structure of DNA has led to renewed hopes of the reduction of biology to chemistry and eventually physics and has provided new opportunities to discuss examples ranging across the natural sciences. It is a simple fact that most university departments of philosophy include at least one or two philosophers who identify themselves either as philosophers of physics or of biology.

But, what about chemistry? One has only to open any general chemistry textbook to see that the subject is presented as a form of applied quantum mechanics. Meanwhile, philosophers of science have become critics of reductionism because according to the formal and logical criteria that they have established, there is no known case of reductionism that goes through in an unproblematic fashion [15]. The reaction to this conclusion from chemists has been one of bafflement or one of completely ignoring such pronouncements as being irrelevant. To make matters worse, many prominent scientists have gone on record as saying that philosophy has absolutely nothing to contribute to science. They include the physicists Stephen Hawking and Steven Weinberg as well as the physical chemist Peter Atkins, in spite of the fact that these authors are rather fond of making philosophical pronouncements about the nature of science.[6]

The philosophy of chemistry is not short of controversial discussions that would benefit greatly from any input from mainstream chemists.[7] A good example of this kind consists on the philosophical claims about the nature of chemical periodicity [16–18]. Other claims by some philosophers of chemistry include the notion that emergence rather than reduction lies at the heart of chemistry [19, 20] or that molecular structure is somehow incompatible with quantum mechanics [21].

Chemical educators tend to have a somewhat unreflective attitude when it comes to understanding the nature of science. I believe that they would be well served by investigating the work published in the philosophy of chemistry and of science in general. Having carried out an informal survey of about 30 US introductory college chemistry textbooks, I can report that not a single one among them presents an account that would be approved of by philosophers of science. In fact, the explanation for the scientific method that is unfailingly trotted out in chemistry textbooks is more than 50 years out of date. These books invariably claim that science begins with observations, which lead almost inexorably to the forming of hypotheses which are then subjected to further experimentation leading in some cases to the development of scientific laws and theories.

Starting in the 1960s and 1970s, this essentially inductive or Baconian account of science in which observation is regarded as the all-important starting point and foundation upon which all of science rests came under severe criticism from philosophers like Karl Popper and Thomas Kuhn [22–24].[8] Positivism has been replaced by the realization that observations are not so untainted and foundational as they were once supposed to be. Instead, it has become appreciated that observations are invariably theory laden. The scientist needs to know what to observe, something that is provided by existing or past theories within any particular domain of science. In addition, the logical status of science or the notion that theories might be proved, or even rendered more probable, by repeated observations has been demolished by Popper's highly influential and now generally accepted views on refutation rather than proof.

Popper's contemporary, Thomas Kuhn, introduced a highly nuanced historical view of the development of science that included his well-known notions of paradigms, anomalies,

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[5] E. Serrelli, entry for Philosophy of Biology in *The Internet Encyclopedia of Philosophy*, http://www.iep.utm.edu/biology/

[6] See for example, P. Atkins, *Galileo's Finger*, Oxford University Press, Oxford, 2004.

[7] M. Weisberg, P. Needham, R. Hendry, Philosophy of Chemistry, in Stanford Encyclopedia of Philosophy, https://plato.stanford.edu/entries/chemistry/. Also see the following critique of the article in E.R. Scerri, Editorial 37, *Foundations of Chemistry*, 13, 1–7, 2011.

[8] First published in 1934 in German as *Logik der Forschung*, first English translation 1959

crises, and revolutions in science. And yet, none of this post-positivist account of the nature of science has yet to make the slightest impact on chemistry or even physics textbooks as far as I am aware.[9]

Not everyone has embraced the views of Popper and Kuhn though, with many thinking that they are flawed and outdated, although to a first approximation, there does appear to be a general consensus on the usefulness of their ideas, which have also formed the basis of much further work. Some have taken Kuhn's views of scientific revolutions to heart as well as his further claim that there is a complete lack of understanding on each side of the revolutionary divide that separates the old paradigm from the one that replaces it. Such incommensurability, as Kuhn has called it, is taken by some to mean that there is no rational way to explain how the successor paradigm takes over from the older one.[10] This apparent vacuum has been filled by some with the notion that social factors dictate why the successor paradigm prevails rather than scientific factors [25]. As is well-known, this line of thinking presents a slippery slope that has led many authors to embrace relativism or to declare the end of science as a privileged path to knowledge.[11] A more modest acceptance of Kuhn's views has prompted yet others to adopt a more naturalistic approach, which supposes that science develops in an evolutionary fashion, something that Kuhn himself hinted at but did not develop in his own writings [26–29].

The even newer approach that I will be discussing in the remainder of this article draws on some elements from Kuhn such as an attention to historical developments combined with an evolutionary epistemology grounded on actual case studies of scientific episodes. In order to present this approach, I will briefly describe the contributions of just one little known individual whose work I believe can illustrate a new vision of the nature of science.[12]

The scientists in question is Antonius van den Broek (1870–1926), who was active in the early years of the twentieth century in the field of atomic structure and who provided a key idea which catalyzed the work of the far the better known Henry Moseley (1887–1915).[13]

The example of Van den Broek

Anton van den Broek never held an academic university position but was an econometrician by profession and had initially trained in the law. It was van den Broek rather than any of the famous profession physicists of the day who first realized that the elements should be ordered according to increasing atomic number rather than atomic weight. I have proposed that van den Broek had the edge on the physicists because of his deep interest in chemistry and the fact that he focused his attention of the periodic table of the elements.[14]

Meanwhile, the leading physicists of the day including Thomson, Rutherford, Barkla, and even Bohr did not concentrate quite so much on the periodic table although some of them did publish early electronic accounts of chemical periodicity [30, 31]. The fact remains that the amateur van den Broek was able to reach a conclusion that had eluded the expert physicists and one which they quickly accepted after he had made it public [32]. The experimental establishment of this view by Henry Moseley is well-known, but as Moseley readily acknowledged in his articles, he undertook his research "with the express purpose of verifying van den Broek's hypothesis."[15]

Here is briefly how van den Broek was the first to arrive at the notion of atomic number. In 1907, he published an article in which he took up a question that Rutherford had recently discussed, namely the nature of α-particles. One of Rutherford's three suggestions was that an α-particle might be half of a helium atom with a charge of twice the hydrogen atom. This idea appealed to van den Broek who coined the term alphon to describe such a particle. He then proposed that such an alphon particle might better serve the role that Prout had intended for the hydrogen atom in his famous hypothesis of 1815. According to van den Broek, the atoms of the elements should therefore consist of a series corresponding to the even whole numbers from 2 up to 240 such that there should be a total of 120 elements, each one made up of a whole number of alphons each with a weight of 2 units.[16] Van den Broek's reason for this proposal rested on experiments by Rutherford and Charles Barkla who had independently concluded that the charge of any atom is approximately half of its atomic weight. Van den Broek just went further in this direction by initially supposing that the relationship was exact and that it applied to all the elements of the periodic table.

At the time van den Broek was writing, there were about 80 known elements and he proposed to populate the remaining 40 or so spots in his new periodic table with new radioactive species that were being rapidly discovered. Van den Broek's

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[9] This situation persists in spite of heroic efforts made by authors in such journals as *Science & Education*, https://link.springer.com/journal/11191

[10] For readers who may not be familiar with Kuhn's term incommensurability, it is intended to mean that some scientific theories (concepts, paradigms, worldviews) separated by a scientific revolution have "no common measure" and cannot therefore be rationally compared.

[11] An early proponent of this view was the philosopher Paul Feyerabend. More recently, it has been championed by certain sociologists of science. H.M., Collins, Stages in the Empirical Program of Relativism – Introduction, *Social Studies of Science*, 11, 3–10, 1981.

[12] E.R. Scerri, *A Tale of Seven Scientists and A New Philosophy of Science*, Oxford University Press, New York, 2016. Other little known chemists and physicists whose work is examined in this book include John Nicholson, Richard Abegg, Charles Bury, John Main Smith, Edmund Stoner, and Charles Janet.

[13] A more detailed version of the work of van den Broek appears in the book cited in reference 21 on which this section has been based.

[14] Ibid, chapter 3.

[15] Ibid, p. 56.

[16] The final element known at the time was uranium whose atomic weight was thought to be 240, thus accounting for the limiting value chosen by Van den Broek.

article of 1907 does not yet show any direct signs of the concept of atomic number, unless one divides each of the atomic weights in van den Broek's table by two to obtain a sequence of values from one to 120 (Table 1). In 1911, van den Broek took a further step toward the concept of atomic number. Building on an obscure passage in an article by Mendeleev, he attempted to design a three-dimensional, or cubic, periodic system (Table 2) as van den Broek described it.

The elements shown diagonally are those that are intended as occupying the third dimension, and curiously, the postulated alphon particle of 1907 is not even mentioned in this article. However, the all-important idea that successive elements differ from each other by 2 U of weight as compared with Mendeleev's and many other periodic tables is retained.

In the same year, van den Broek published a remarkably short and suggestive statement in *Nature* magazine. It is here that we can begin to see the concept of atomic number taking a definite shape. Van den Broek repeats the fact that two independent lines of experimentation, due to Rutherford and Barkla, respectively, have pointed to the simple and approximate relationship between the charge on an atom and its atomic weight, namely,

$$\text{charge} \approx A/2$$

By reference to his new 'cubic' table and his prediction that a total of 120 elements should exist, van den Broek concludes by saying,

> If this cubic periodic system should prove to be correct, then the number of possible elements is equal to the number of possible permanent charges of each sign per atom, or to each possible permanent charge (of both signs) per atom belongs a possible element.

Stated otherwise, van den Broek is suggesting that since the charge on an atom is half of its atomic weight, and since the weights of successive elements differ by 2 units in a stepwise fashion, the charge on an atom defines its position in the periodic table. Neither Rutherford, Barkla, nor anybody else had considered the elements in the periodic table as a whole, and consequently, they had missed this key point, whereas Rutherford and Barkla recognized that

$$\text{charge} \approx A/2$$

van den Broek went further in seeing that,

$$\text{charge} \approx \ A/2 \ = \ \text{atomic number}$$

Just as the 1911 article involved the abandonment of the alphon particle, the next article (of 1913) involved the abandonment of the cubic periodic table. I firmly believe that this kind of incremental thinking is the rule rather than the exception in the growth of scientific knowledge [33].

In 1913, the cubic table was replaced by a two-dimensional system, shown in Table 3. Van der Broek now also made a clearer statement in which a serial number for each element is first announced.

> The serial number of every element in the sequence ordered by increasing atomic weight equals half the atomic weight and therefore the intra-atomic charge.

Table 1 Van den Broek's periodic table of 1907

	VII	0	I	II	III	IV	V	VI
1	2* (α)	4 He	6 Li	8 Be	10 B	12 C	14 N	16 O
2	18 F	20 Ne	22 Na	24 Mg	26 Al	28 Si	30 P	32 S
3	34 Cl	36 Ar	38 K	40Ca	42 Sc	44 Ti	46 V	48 Cr
4	50 Mn	52	54	56 Fe	58 Co	60 Ni	62	64
5	66	68	70 Cu	72 Zn	74 Ga	76 Ge	78 As	80 Se
6	82 Br	84 Kr	86 Rb	88 Sr	90 Y	92 Zr	94 Nb	96 Mo
7	98	100	102	104 Ru	106 Rh	108 Pd	110	112
8	114	116	118 Ag	120 Cd	122 Jn	124 Sn	126 Sb	128 Te
9	130 J	132 Xe	134 Cs	136 Ba	138 La	140 Ce	142 Nd	144 Pr
10	146	148	150 Sa	152	154 Gd	156	158 Tb	160
11	162	164	166 Er	168 Tu	170 Yb	172	174 Ta	176 W
12	178	180	182	184 Os	186 Ir	188 Pt	190	192
13	194	196	198 Au	200 Hg	202 Tl	204 Pb	206 Bi	208
14	210	212	214	216	218	220	222	224
15	226	228	230	232 Ra	234	236 Th	238	240 U

*Theoretical atomic weight

Table 2 Van den Broek's cubic periodic table of 1911

		0			I			II			III			IV			V			VI			VII		
		1	2	3	1	2	3	1	2	3	1	2	3	1	2	3	1	2	3	1	2	3	1	2	3
A	1	He			Li			Be			B			C			N			O			F		
	2		Ne			Na			Mg			Al			Si			P			S			Cl	
	3			Ar			K			Ca			Sc			Ti			V			Cr			Mn
B	1	Fe			Co			Ni			Cu			–			–			–			Zn		
	2		–			–			–			Ga			Ge			As			Se			Br	
	3			Kr			Rb			Sr			Y			Zr			Nb			Mo			Ru
C	1	Rh			Pb			–			–			Ag			–			–			Cd		
	2		–			–			–		In				Sn			Sb			Te			J	
	3			Xe			Cs			Ba			La			Ce			Nd			Pr			(Sm)
D	1	(Eu)			(Gd$_1$)			(Gd$_2$)			(Gd$_3$)			(Tb$_1$)			(Tb$_2$)			(Dy$_1$)			(Dy$_2$)		
	2		(Dys)			(Ho)			(Er)			(Tu$_1$)			(Tu$_3$)			(Tu$_3$)			(Yb)			(Lu)	
	3			–			–			–			–			–			Ta			W			Os
E	1	Ir			Pt			Au			Hg			Ti			Bi			Pb			–		
	2		–			–			–			–			–			–			–			–	
	3			–			–			Ra			–			Th			–			U			–

Table 3 Geiger and Marsden. Ratio of scattering of α-particles per atom in several elements

I Substance	II Air equivalents of foils used	III Total number of scintillations Counted for each substance	IV Number N of scintillations at same angle and for same air equivalent	V $A^{3/2}$	VI $N/A^{3/2}$
Gold………..	.52, .68	1200	2400	2770	.85
Platinum…	.54, .625	1000	2900	2730	1.08
Tin………….	.51, 1.51	1400	1290	1300	.99
Silver………	.38, .435	600	1060	1120	.95
Copper…….	.495, .61	1300	570	507	1.12
Aluminum.	.45, .52, 1.06	1600	151	144	1.05
Carbon…….	.55, .57	400	57	41.6	1.37

This article was cited by Niels Bohr in his trilogy paper of the same year, 1913, the work that traditionally marks the birth of the quantum theory of the atom.

Perhaps, the most significant development took place in another article that van den Broek placed in *Nature* magazine in which he abandoned the connection with atomic weight altogether. Van den Broek began with a set of experiments by Hans Geiger and Ernest Marsden, aimed at examining the ratio of scattering of α-particles per atom in several elements (Table 3).

According to Rutherford, this ratio needed to be constant, but this is not what Geiger and Marsden found when they divided the scattering by the atomic weight of each element [34]. Nevertheless, Geiger and Marsden were not concerned about this discrepancy, believing that the error was small and could be ignored. Meanwhile, van den Broek got to work trying to make the ratio more constant. He achieved this by dividing the amount of scattering for each element by its charge rather than by its atomic weight. On doing this, he found that the ratio was closer to being a constant thus reinforcing the notion that charge was a more important criterion for identifying any element than atomic weight.

Table 4 Rather than the representation chosen by Geiger and Marsden, the order of the elements has been inverted to show increasing atomic weights from *top* to *bottom*. Condensed by the present author

Element	A	$N/A^{3/2}$
Al	27.1	0.24
Cu	63.57	0.23
Ag	107.88	0.18
Sn	119	0.21
Au	197.2	0.21

Table 5 Geiger and Marsden's experiments on the degree of scattering in various metals

Element	Scattering per atom/A^2 Experiment 1	 Experiment 2
Cu	3.7	3.95
Ag	3.6	3.4
Sn	3.3	3.4
Pt	3.2	3.4
Au	3.4	3.1

Table 6 Van den Broek's scattering ratios for several metals

	Cu	Ag	Sn	Pt	Au	Mean
Scattering/(A^2/5.4)	20.6	18.9	18.1	17.8	17.5	18.6
M	29	47	50	82	83	
Scattering/M2	18.5	18.4	19.0	18.6	18.4	18.6

In a section of their 1913 article, Geiger and Marsden investigated the variation of α-particle scattering with the atomic weight of a number of elements. They reported the following values (Table 4) for the number of scintillations per centimeter of equivalent air multiplied by atomic weight raised to the power of 3/2. Geiger and Marsden then immediately stated,

> This ratio [N/A$^{3/2}$] should be constant according to the theory. The experimental values show a slight decrease with atomic weight.[17]

Once again, such disagreement between theory and experimental data did not seem to disturb Geiger and Marsden too much. In a couple of footnotes, Geiger and Marsden also reported experiments in which they obtained the ratio of scattering per atom divided by the square of the atomic weight of an almost identical set of elements (Table 5).

This was followed by,

> These results are similar, and indicate the essential correctness of the assumption that the scattering per atom is proportional to the square of the atomic weight, the deviations from constancy of the ratio are nearly within experimental error.[18]

Van den Broek was already starting to think that charge was a better criterion for explaining questions regarding the periodic table and the structure of the atom. He was now in a position to support this notion by drawing on Geiger and Marsden's data. He began by dividing the scattering per atom by the square of the charge of an atom instead of the square of its atomic weight. By doing so, he found that the constancy predicted by Rutherford was more accurately recovered. In the same table, he displayed values for scattering divided by A^2/5.4, where the purpose of the factor of 5.4 is simply to render the ratios based on M^2 comparable to those using A^2 (Table 6).

Table 7 Table that appears in van den Broek's *Nature* article of November 27, 1913. The final column has been added by the present author

Element	Mean	Mean × 5.4	Mean × A^2/M^2	M	A
Cu	3.825	20.6	18.4	29	63.57
Ag	3.5	18.9	18.4	47	107.88
Sn	3.35	18.1	19	50	119
Pt	3.3	17.8	18.7	82	195.2
Au	3.25	17.5	18.3	83	197.2

In the second article, the same exercise was repeated in a more transparent manner that shows the two sets of data from Geiger and Marsden. Van der Broek's conclusion was exactly as it was in the first of these two articles, namely that the scattering data only agree with Rutherford's theory provided that charge is considered rather than atomic weight (Table 7) [35]. Only now was van den Broek ready to take the decisive step of severing the connection between atomic weight and charge or atomic number.

> If now in these values the number M of the place each element occupies in Mendeléeff's series is taken instead of A, the atomic weight, we get a real constant (18.7 +/− 0.3); hence the hypothesis proposed holds good for Mendeléeff's series, but the nuclear charge is not equal to half the atomic weight.[19]

Conclusion

And the rest, as the saying goes, is history. In a couple of now very famous articles, Henry Moseley at Manchester and then Oxford conducted his experiments that provided confirmation of van den Broek's hypothesis. The influence of van den Broek's work on that of Moseley is in no doubt whatsoever since Moseley begins his articles by stating that he is setting with the express purpose of verifying van den Broek's hypothesis, as mentioned earlier. *This is just one of numerous examples of the*

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[17] Ibid.

[18] Ibid, p. 619,

[19] Ibid. Table appears on p. 373.

gradual and evolutionary development of a scientific concept that I suggest is the rule rather than the exception. The development occurs in an almost random fashion although each step also benefits from rational decisions on the part of the scientist as to what to follow up and what to abandon. More importantly perhaps, subjecting new ideas to experimentation plays the role that the environment plays in biological evolution, when it comes to the survival or otherwise of a scientific concept. The overall development is non-teleological and involves far more chance, serendipity, and just trying things out and a correspondingly smaller role for rationality and intentional design [36].

Moreover, I have argued that "little people" such as van den Broek are just as important as the heroes of science such as Moseley in the overall scheme of things. Science does not proceed via sharp revolutions as Kuhn famously claimed but rather in an incremental fashion to which all kinds of scientist at various levels contribute. Seen in this light questions of priority disputes and whether or not multiple discoveries occur become less important or perhaps are more easily explained [37, 38]. Priority disputes may matter to the individuals concerned, but the progress of science as a whole could not care less.[20]

Rather than trying to tell chemists how to interpret their theories as some philosophers of chemistry have tried to do, I prefer a role for philosophers in which they closely study scientific episodes. Such an approach often succeeds in filling in the missing steps and of countering the traditional stories of scientific heroism on the part of a few highly gifted individuals. This more modest image of the development of science can also serve to counter the widely held view that scientists are elitists who should be marginalized by politicians and society at large.[21]

Compliance with ethical standards

Conflict of interest I declare that there is no conflict of interest.

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