

The van den Broek Hypothesis

Tetu HIROSIGE*

1. Introduction

In the development of the study of the atomic structure during the 1910's, the foundation of models of the atom was provided by van den Broek's hypothesis. The van den Broek hypothesis states that the electric charge of the nucleus or the number of intra-atomic electrons of a chemical element is equal to its ordinal number in the periodic system. Once the hypothesis was proposed by A. van den Broek in 1913, it exerted considerable influence upon N. Bohr, H. G. J. Moseley, and F. Soddy and was soon accepted by most of those who were interested in the atomic physics. This rapid acceptance may presumably be accounted for by the fact that it was just the time when various inquiries into the number of intra-atomic electrons were converging to a nearly correct conclusion. No settled conclusion, however, had yet been pronounced. The van den Broek hypothesis gave a clear and definite expression to this vaguely felt conclusion, and thus greatly advanced the atomic physics. To attach an essential significance to the atomic number was van den Broek's most original idea, which had occurred to no one before him.

E. Whittaker, in his *History of the Theories of Aether and Electricity II*, wrote about the van den Broek hypothesis as though it were originated in an examination of experimental results of α -particle scattering.¹ According to the Rutherford formula, the number of particles scattered by an atomic nucleus to a given angle is proportional to the square of the nuclear charge. H. Geiger and E. Marsden in 1913 carried out careful experiment and concluded that the Rutherford formula would be approximately fulfilled if the nuclear charge was assumed to be half the atomic weight.² "But van den Broek now," says Whittaker, "pointed out that it would be satisfied with far greater accuracy if the nuclear charge were assumed to be proportional to the number representing the place of the element in the Newlands-Mendeleev periodic table."

Whittaker's account, however, is somewhat misleading. For, first, van den Broek proposed his hypothesis in its original form not after, but before the result of Geiger and Marsden's experiment was published. The paper in which van den

* Department of Physics, College of Science and Engineering, Nihon University, Kanda Surugadai, Tokyo, Japan.

¹ E. Whittaker, *A History of the Theories of Aether and Electricity, II* (London, 1953), pp. 23-24.

² H. Geiger and E. Marsden, "The Laws of Deflexion of α -Particles Through Large Angles," *Phil. Mag.* (6), **25**, 604-623 (April 1913).

Broek put forward the hypothesis was received on November 15, 1912 and was published on the 1 January, 1913 issue of *Physikalische Zeitschrift*,³ whereas Geiger and Marsden's paper was published on the April 1913 issue of *Philosophical Magazine*. Moreover, if we seek the germ of the hypothesis, we find it to have appeared as early as in 1911. Second, van den Broek initially put forward his hypothesis not by suggestion from the α -particle scattering, but in connection with his effort to construct comprehensive periodic system. In the following, I propose to investigate the process by which the van den Broek hypothesis gradually took shape, and the reaction of the contemporary physicists to this hypothesis.

2. General Background

Before entering the actual origin of van den Broek's hypothesis, it will be convenient to throw a glance over the general situation of the theory of the atomic structure during 1911–13.

Cursory investigation over abstract journal such as *Science Abstract—Section A, Physics* reveals that there were rather few papers dealing with the structure of the atom, and that the Thomson model had not yet faded away in this period. At the British Association meeting in September 1913, where J. H. Jeans appraised Bohr's theory of the atomic constitution with great favour and thus made it publicly recognized for the first time in the scientific community, J. J. Thomson, on the one hand, opposed Rutherford's theory of single scattering, and, on the other, presented an attempt to derive the energy quantum from the structure of the atom.⁴ As for the α -scattering, he asserted that it would be accounted for by deviation of the law of electric force from the inverse square law at very short distance. For the purpose of deducing the energy quantum, he assumed that in the interior of an atom the electric force, instead of acting everywhere throughout the atom, was confined within a finite number of tubes of force. Though this model indeed differs from the simple positive sphere model of 1904, it may well be reckoned as a variation of that model insofar as the electrons are assumed to distribute themselves within a sphere of the opposite electric charge.

Thomson was not alone in adhering to the Thomson model. There were others who also made speculation based on the Thomson model. For example, in 1911 H. A. Wilson considered, on the basis of the Thomson model, a possible relation between the number of electrons in an atom and its atomic weight.⁵ Another example is K. F. Herzfeld's attempt in 1912 to account for the Balmer series by applying the quantum condition proposed by F. Hasenöhr!⁶:

³ A. van den Broek, "Die Radioelemente, das periodische System und die Konstitution der Atome," *Phys. Zeits.*, **14**, 32–41 (Jan. 1913).

⁴ J. J. Thomson, "On the Structure of the Atom," *Phil. Mag.* (6), **26**, 792–799 (Oct. 1913).

⁵ H. A. Wilson, "The Number of Electrons in the Atom," *Phil. Mag.* (6), **21**, 718–722 (June 1911).

⁶ F. Hasenöhr!, "Über die Grundlagen der mechanischen Theorie der Wärme," *Phys. Zeits.*, **12**, 931–935 (Nov. 15, 1911).

$$\int_{E_s}^{E_{s+1}} \tau dE = h$$

to the motion of electron inside the positive sphere of the Thomson model.⁷

It should be noted, however, that an approach was also being made from the part of the Thomson model to the conception that the atom had a kind of "core". During February and March 1913, Thomson gave a course of lectures⁸ in which he remarked that the characteristic X-rays radiated out from an element was not affected by whether or not the element was combined with other elements. This, he thought, indicated that the characteristic X-rays were emitted from the inner part of the atom which was hardly affected by chemical combination. Thus Thomson concluded that the atom would consist of outer corpuscles (electrons), which determined its chemical properties, and the central core.

On the other hand, not until Bohr's theory of 1913 the implication of Rutherford's model had been grasped to its full extent. Rutherford himself, at first, thought the originality of his theory to consist rather in its regarding the α -scattering as single in opposition to Thomson's regarding it as compound, than in the "nuclear" model.⁹ It is true that Rutherford used a model which differed from Thomson's in its assuming a strong centre of force in the atom. But at the same time, the centre of force was assumed to be surrounded by a uniform sphere of an opposite electric charge and, even more, a possibility was admitted that a number of electrons dispersed themselves throughout this sphere. The model conceived by Rutherford at this time might therefore be considered a special case of the Thomson model which is obtained by collecting a part of electrons to the centre of the positive sphere. Rutherford seems not to have been clearly aware that his model drastically opposes itself to the Thomson model. This suspicion is corroborated by the interview with Bohr conducted by the Sources for History of Quantum Physics project. Bohr then told that at Manchester no one was thinking of positive nucleus and surrounding electron rings.¹⁰

This being admitted, it would then be asked why the words "Structure of the Atom" was inserted in the title of Rutherford's 1911 paper.¹¹ It might not be impossible to interpret this as indicating the existence of the centre of force. But Rutherford at that time was primarily concerned to claim the singleness of the α -scattering, and the centre of force was subordinated to this claim. It seems more

⁷ K. F. Herzfeld, "Über ein Atommodell das die Balmer'sche Wasserstoffserie aussendet," *Sitzb. Akad. Wiss. Wien*, **121**, 593-601 (April 1912).

⁸ J. J. Thomson, "The Structure of the Atom," *The Electrician*, **70**, 1096-1097; 1133-1135 (March 21, 28, 1913).

⁹ S. Nisio, " α -Rays and the Atomic Nucleus", *Jap. Stud. Hist. Sci.*, No. 4 (1965), 91-116. John L. Heilbron, "The Scattering of α and β Particles and Rutherford's Atom", *Arch. Hist. Exact Sci.*, **4**, 247-307 (1968).

¹⁰ Interview with Bohr by the History of Quantum Physics Project. Session 3, Nov. 7, 1962.

¹¹ E. Rutherford, "The Scattering of α and β Particles by Matter and the Structure of the Atom" *Phil. Mag.* (6), **21**, 669-688 (May 1911).

reasonable to interpret it as referring to the value of the central charge. The sixth section of the paper bearing the title "Comparison of Theory with Experiments" occupies nearly one third of the total pages of the paper. Rutherford there examined the value of the central charge deduced from the α - and β -scatterings. He began this section with the words: "On the present theory, the value of the central charge Ne is an important constant, and it is desirable to determine its value for different atoms."¹² The result Rutherford obtained was that the central charge was roughly proportional to the atomic weight and was about $100e$ for gold.

That the determination of the central charge was one of the most important problems for Rutherford may well be seen from the fact that in Geiger and Marsden's 1913 paper,¹³ which was devoted to verification of the Rutherford formula, special attention was paid upon the evaluation of the central charge. Geiger and Marsden first confirmed that the number of scattering per atom into a given angle was proportional to the square of the atomic weight, and then counted the absolute number of scattering for gold. Combining both these results, they concluded that the central charge was equal to half the atomic weight. They repeated, under two different conditions, the experiment to confirm the relation between the number of scattering with the square of the atomic weight "on account of the importance of these experiments."¹⁴

By this time, the conclusion that the intra-atomic charge was roughly equal to half the atomic weight had also been reached by investigations on different lines. In 1906 J. J. Thomson found by three different methods that the number of intra-atomic electron was of the order of the atomic weight.¹⁵ In 1910 J. A. Crowther¹⁶ analyzed in terms of Thomson's theory of compound scattering¹⁷ the result of β -ray scattering experiment of his own and concluded that the number of the intra-atomic electrons was about three times of the atomic weight. In the next year C. G. Barkla tried to estimate the number of the intra-atomic electrons by examining the scattering of X-rays by matter.¹⁸ He obtained the result that for lighter atoms of atomic weight not larger than 32, the number of electrons was about half the atomic weight.

The consideration above allows us to conclude that those who were interested in the structure of the atom at the beginning of 1910's focussed their attention to experimental determination of the number of the intra-atomic electrons, and that the results obtained by different methods were converging to the value $1/2 A$, half

¹² *Ibid.*, p. 680.

¹³ H. Geiger and E. Marsden, *op. cit.* (2).

¹⁴ *Ibid.*, p. 618.

¹⁵ J. J. Thomson, "On the Number of Corpuscles in an Atom," *Phil. Mag.* (6), 11, 769-781 (June 1906).

¹⁶ J. A. Crowther, "On the Scattering of Homogeneous β -Rays and the Number of Electrons in the Atom," *Proc. Roy. Soc.*, A84, 226-247 (1910).

¹⁷ J. J. Thomson, "On the Scattering of Rapidly Moving Electrified Particles," *Proc. Camb. Phil. Soc.*, 15, 465-471 (1910).

¹⁸ C. G. Barkla, "Note on the Energy of Scattered X-radiation," *Phil. Mag.* (6), 21, 648-652 (May 1911).

the atomic weight. It was with this problem which was attracting much attention of contemporary physicists that the van den Broek hypothesis was concerned. Moreover, the hypothesis was put forward in the form that made plain what most of the physicists had, consciously or unconsciously, in mind.

3. Path to the Hypothesis

Antonius van den Broek was born in Zoeterwoude in the Netherlands on May 5, 1870 and died in Bithoven on October 26, 1926.¹⁹ He was a lawyer in profession and an amateur scientist as well. He was not affiliated with any scientific society but, as we shall see in the following, was well acquainted with informations in physics of the day. His seemingly first scientific paper that was recorded on abstract journal was "The α -particle and the Periodic System of Elements" published in 1907.²⁰ The first step to his hypothesis was already taken in this paper.

In 1906 Rutherford, having determined the specific charge of the α -particle, enumerated three possibilities with regard to the nature of the α -particle.²¹ They were hydrogen molecule with a single charge, doubly ionized helium atom, and half-atom of helium with a single charge, of which he excluded the first on the ground of its lesser stability. He however refrained from deciding between the remaining two. Van den Broek took inspiration from this consideration of Rutherford's. Stating that where experiment could not decide there still remained pure speculation, he ventured a speculation about the periodic table. His fundamental idea was to suppose what Rutherford called half-atom of helium to be the primordial matter, which was to take the place of hydrogen in Prout's hypothesis. Naming this half-atom *alphon*, he supposed that to each number of aggregated alphons corresponded an independent chemical element. Consequently all the even numbers from 2 (= alphon) to 240 (= uranium) would represent the atomic weights of possible chemical elements. Total number of the elements would then become larger than the number of the known elements. Van den Broek thought, however, that this would be rather convenient in view of the newly discovered radioactive products, which so far had not been determined where to be placed in the periodic system. He assigned one period to each of the rare earth group and three groups of transient metals respectively. Accordingly the periodic table he constructed consisted of fifteen rows and eight columns. He claimed that his table had the merit that irregularities in the generally accepted tables disappeared there. He further emphasized that the theoretical atomic weights assigned to known elements according to their places in his table little differed from their experimentally determined values, the

¹⁹ H. A. Boorse and L. Motz, *The World of the Atom*, 2 vols., New York, 1966. See vol. 1, p. 855. I have thus far not been able to find another published biographical information about van den Broek.

²⁰ A. van den Broek, "Das α -Teilchen und das periodische System der Elemente," *Ann. d. Phys.* (4), **23**, 199-203 (1907).

²¹ E. Rutherford, "The Mass and Velocity of the α -Particles Expelled from Radium and Actinium," *Phil. Mag.* (6), **12**, 348-371 (Oct. 1906).

TABLE 1

	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	40 Ca	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.

mean difference being 0.06%.

In view of later development of his thought, it is interesting to note that van den Broek here put forward the conception that "the elements are merely secondary variations of conglomeration of α -particles (secundäre Abänderungen von α -Teilchenkonglomerationen)."²² From this conception the conclusion may follow that to each of even numbers corresponds a possible chemical element, which in turn implies that the difference of atomic weights of two adjacent elements, if all the possible elements are taken into account, should be, in mean, equal to 2. Though he did not explicitly draw this conclusion in the 1907 paper, it would always lie at the root of all his later speculation.

Here it may be helpful to sketch the general situation of the periodic system at the time. Though the periodic system of Mendeleev was discovered as early as in 1869, it could not take a definite shape before the Bohr theory of the atomic structure was sufficiently developed after 1913. Difficulties were caused particularly by the rare earth elements and the radioactive products. The last member, apart from the synthesized promethium, of the rare earths, lutetium, was discovered in 1907. But before Moseley's work of 1913-14, there was no conclusive method of separating and identifying different elements. It was not until 1922, when Bohr put forward his theoretical explanation of the periodic system, that the rare earths were satisfactorily incorporated into the periodic system.²³

²² A. van den Broek, *op. cit.* (20), p. 203.

²³ J. W. van Spronsen, *The Periodic System of Chemical Elements. A History of the First Hundred Years* (Elsevier, Amsterdam-London-New York, 1969), p. 274.

As for the radioactive products, particularly for the post-emanation members, their chemical properties were still quite vague. The post-emanation members seemed not to resemble any known element.²⁴ It was by the discoveries of the concept of isotope and the displacement law that the radioactive products became possible to be incorporated into the periodic system on firm basis. These concept and law were discovered at the beginning of 1913, almost simultaneously with and independently of the van den Broek hypothesis. It is to be noted that, as we shall see later, their establishment and clarification were rather promoted by the latter hypothesis.

Van den Broek's hypothesis emerged from such an ambiguity of the periodic system as sketched above. The ambiguity induced him to attempt at constructing a more satisfactory periodic system. And it was by taking advantage of this ambiguity that he could frame his hypothesis.

Van den Broek's second proposal of periodic system appeared in 1911.²⁵ He noted that Mendeleev's system had not satisfied sufficiently the requirement of periodicity, and that Mendeleev himself, being aware of the incompleteness of his system, intended to construct a second type of the system in which the elements would be arranged three-dimensionally. It was not possible for Mendeleev actually to make such a system because too few elements were then known for this purpose.

TABLE 2

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

²⁴ F. Soddy, "The Origins of the Conceptions of Isotopes," *Nobel Lectures. Chemistry 1901-1921* (Elsevier, Amsterdam-London-New York, 1966), 371-399. The quotation is on p. 385.

²⁵ A. van den Broek, "Das Mendelejeffsche 'Kubische' Periodische System der Elemente und die Einordnung der Radioelemente in dieses System," *Phys. Zeits.*, **12**, 490-497 (15. Juni, 1911).

Now that, however, many rare earth elements and radioactive products had been discovered, it would be possible, thought van den Broek, to realize Mendeleev's intention. He regarded each of the three groups of transient metals and the rare earth group as an independent period respectively, according to the conception he had held since his first attempt in 1907. Then he piled up three rows, each consisting of eight places, one over another, and arranged five blocks thus formed one next to another. This "cubic" system, as van den Broek called, is able to comprise $8 \times 3 \times 5 = 120$ elements, and may be regarded essentially as a slightly modified version of the 1907 system. The 15 rows in the previous system now are divided into 5 sub-groups, each consisting of 3 rows piled up one upon another. But the alphon has disappeared, some of the elements are displaced to the left or right, and a number of rare earths and radioactive products have been added.

Van den Broek admitted that the cubic system was inferior to Mendeleev's original system in clarity and had left a good many vacant places. He, however, emphasized that his system had merits of its own. First, there is always one element in one place. Second, all the rare earths and radioactive products can easily be incorporated in the system. Third, all the periods have equal length, eight. Last but of special importance to our concern is that the mean difference of the atomic weights of any two adjacent elements is constant, and equal to two. In the generally accepted periodic systems, two mean differences about 2 and 4 appear alternatively. For example, the mean difference for thirty elements from He through Zn is 2.13, whereas that for five elements from Zn through Se is 3.46. The mean difference for fifteen elements from Se through Ag is 2.05, and so on. In his new system, this lack of uniformity may be remedied by taking into account the many vacant places. For example, there are six places between Zn and Se in his cubic system. The difference of the atomic weights of Se and Zn, 13.8, therefore, should be divided not by 4 but by 7. Then 1.83 is obtained as the mean difference. If, in this way, theoretical atomic weight is assigned to each known elements, then the mean deviation of the theoretical value from the measured value of the atomic weight proves to be nearly zero (the mean relative deviation = 0.3%). Additional support for the theoretical atomic weight is supplied, asserted van den Broek, by the fact that the difference of the atomic weights of an α -emitting element and its product is twice the mean difference 2 and, at the same time, the atomic weight of the α -particle too is twice the mean difference.

In the previous paper van den Broek assumed a series of possible elements on the supposition that atoms of all the elements consisted of hypothetical "alphons." He then distributed actual elements over that series in such a way that their atomic weights got best accorded with appropriate theoretical atomic weights. The mean difference 2 was a logical consequence of the constructing principle of the system. In contrast to this, the problem in the 1911 paper was how to arrange the actual elements so as best to fit the periodic law. Here the mean difference 2 was a contingent result from the periodic system constructed in this way. The constructing

principles of the two system were quite different. Nevertheless, the conception that the atomic weights corresponded to continuous series of even numbers was inherited from the 1907 paper to the 1911 paper. And it appears that this conception also suggested to him the idea that all the atoms, in the main, consisted of α -particles. For he emphasizes, as mentioned above, that the emission of an α -particle corresponds to a change of atomic weight by twice the mean difference 2. As we shall see later, the conception that the major constituent of the atom is the α -particle continues to be the keynote of his speculations.

The paper proposing the cubic periodic system was received on April 16, 1911. About three months later, van den Broek sent to the 20 July issue of *Nature* a letter of less than 200 words, in which he for the first time discussed the number of intra-atomic electrons.²⁶ This letter was motivated by the two papers of Rutherford and of Barkla, both published on the May issue of *Philosophical Magazine*. As was mentioned in the foregoing, in both these papers the number of intra-atomic electrons was concluded, by entirely different methods, to be nearly equal to half the atomic weight. If this conclusion is admitted, the number of electrons contained in the uranium atom must be some 125. Now in the cubic periodic system the number of possible elements amounts to 120. It may therefore be concluded, asserted van den Broek, that "to each possible permanent charge (of both signs) per atom belongs a possible element."

Provided the cubic system is presumed, this conclusion evidently implies the proposition that the atomic number is equal to the intra-atomic charge. But at this moment van den Broek was still unaware of this. He at least did not mention it explicitly. It was toward the end of 1912, and in the paper submitted to *Physikalische Zeitschrift*²⁷ that he positively stated that proposition.

4. The Hypothesis Stated

Van den Broek's renewed effort in 1912 to construct a periodic system was motivated by progress in the research of the radioactivity. During 1911-12, thanks mainly to the efforts of the Rutherford group, it was definitely shown that the substances which had been thought to emit two α -particles simultaneously, *i.e.* uranium, thorium emanation, and actinium emanation, in fact emitted only a single α -particle, and that the disintegrations of substances such as U, RaC, and ThB were compound and branchings of radioactive series ensued. These results seemed to van den Broek to suggest that disintegration products having equal atomic weight were to be considered one and the same element. For, unless this was admitted, the complex disintegration would compel us to assume too numerous new elements. He also thought that, due to the result that all the α -emitters radiate a single particle each, it would become possible to calculate the atomic weight of a radioactive pro-

²⁶ A. van den Broek, "The Number of Possible Elements and Mendeleeff's "Cubic" Periodic System," *Nature*, 87, 78 (July 20, 1911).

²⁷ *Op. cit.* (3).

duct, provided that its order on the radioactive series was known. Thus he proposed to determine the arrangement of radioactive elements on the periodic system on the basis of their atomic weight.

The view outlined above lead him to the conclusion that each α -disintegration decreased the atomic weight of the radioactive substance by four and transformed it into another substance. β -disintegration, on the other hand, would not alter the atomic weight. Van den Broek, following Ramsay, assumed the product of β -disintegration to be secondary form of an α -active element having the same atomic weight as that product. Having in this way drawn up genealogies of each of three radioactive families, he now tried to incorporate them into the periodic system. Chemical analogies were fully used as a guide. It then turned out necessary to put more than one elements in one and the same place belonging to the groups 0 and III. This was not to be rejected in principle, however, because, argued he, there had been placed three elements such as Fe, Co, and Ni in one place of the VIIIth group. Even more, he considered it convenient, in order to incorporate all the radioactive substances, to put triplet elements in the places of the eighth column which had been left vacant in the current periodic system. In addition to this, he also proposed to extend the complexity of 0th, IIIrd, and VIIIth groups to lighter elements for the reason that the number of rare earth elements was increasing.

The alleged merit of the systems of 1907 and 1911 that to each one place belongs

TABLE 3

0	I	II	III	IV	V	VI	VII	VIII			
2* He	3 Li	4 Be	5 B	6 C	7 N	8 O	9 F				
	10 Ne	11 Na	12 Mg	13 Al	14 Si	15 P	16 S	17 Cl			
18 —	19 Ar	20 K	21 Ca	22 23 Sc —	24 Ti	25 V	26 Cr	27 Mn	28 Fe	29 Co	30 Ni
		31 Cu	32 Zn	33 Ga	34 Ge	35 As	36 Se	37 Br	38 —	39 —	40 —
41 —	42 Kr	43 Rb	44 Sr	45 46 Y —	47 Zr	48 Nb	49 Mo	50 —	51 Ru	52 Rh	53 Pd
		54 Ag	55 Cd	56 In	57 Sn	58 Sb	59 Te	60 J	61 —	62 —	63 —
64 —	65 Xe	66 Cs	67 Ba	68 69 La —	70 Ce	71 Nd	72 Pr	73 —	74 Sa	75 Eu	76 Gd
		77 Tb	78 (Tb ₂)	79 Dy	80 Ho	81 Er	82 Ad	83 AcC	84 TuI	85 TuII	86 AcA
87 —	88 AcEm	89 AcX	90 TuIII	91 92 RAc Cp	93 Ct	94 Ta	95 Wo	96 —	97 Os	98 Ir	99 Pt
		100 Au	101 Hg	102 Tl	103 Pb	104 Bi	105 RaF	106 ThC	107 RaC	108 ThA	109 RaA
110 ThEm	111 RaEm	112 ThX	113 Ra	114 115 RTh Io	116 Th	117 UII	118 U	119 —	120 —	121 —	122 —

* Atomic number.

one element each has disappeared here. But van den Broek did not worry himself at all about this. He felt happy to have obtained the mean difference of two adjacent elements which again had proved to be two. He emphasized that the mean difference could be made equal to two by increasing the number of places in the periodic system, and that to each element could be assigned a theoretical atomic weight, which differed, in average, very slightly (0.22%) from the actual atomic weight. He pointed out that the regularity of the mean difference two which had been recognized at the top part of the periodic system was extended to the whole system, and said that "in view of this, the modification of the periodic system here proposed has rather the significance that by it the regularity is increased . . . and also a meaning more than that."²⁸ What he called "a meaning more than that" was nothing else but the hypothesis with which we are concerned here.

He noted that Barkla and Rutherford had independently concluded the number of intra-atomic elements to be about half the atomic weight. This result shows that "to each element should be ascribed an intra-atomic charge (of both signs) which differs from an element to another." Moreover, combined with the mean difference 2 of atomic weights, it implies that "to each element should be ascribed an intra-atomic charge which is equal to the number representing the order of that element, that is, to the n -th element n intra-atomic charges of both signs."²⁹ As for $n = 1$ and 2, that is, hydrogen and helium, J. J. Thomson had confirmed on his investigation of positive rays that these two elements could not be electrified beyond 1 and 2 elementary charges respectively.³⁰ Referring to this result van den Broek remarked that it exactly corresponded to his conclusion.

From the description above it is evident that it was not the ordinal number of element in Mendeleev's periodic system that van den Broek asserted to be equal to the intra-atomic charge. As for hydrogen and helium experimental fact had suggested that the ordinal number in Mendeleev's system was equal to the intra-atomic charge. He could cite this as supporting in part his hypothesis. But with regard to the other elements, heavy elements in particular, the ordinal number used by him was not the number in the generally accepted periodic system. It was the number in the system composed by him so that the ordinal number of element would be equal to half the atomic weight. Van den Broek's hypothesis, therefore, stated no more than that the intra-atomic charge was equal to half the atomic weight, the conclusion which had been reached by Rutherford's, Barkla's, and others' experiments. Thus he at this stage did state nothing new about the value of the intra-atomic charge itself. What was new with him was the enlargement of the periodic system in such a way that the ordinal number of an element would become equal to half the atomic weight, that is, the intra-atomic charge accepted by most of the contemporary physicists.

²⁸ *Ibid.*, p. 35.

²⁹ *Ibid.*, p. 39.

³⁰ J. J. Thomson, "Further Experiments on Positive Rays," *Phil. Mag.* (6), 24, 209-253 (Aug. 1912), esp. pp. 235-237.

Such a modification of the periodic system had continually been pursued by him since 1907. It was precisely because there remained uncertainties about the periodic system that he repeatedly attempted to compose modified versions of the periodic system. So long as the periodic table had not finally been settled, there naturally was no definite atomic number. But because of this absence of the atomic number, van den Broek was able to make up such a periodic table that the atomic number on it would be equal to the intra-atomic charge which was generally inferred at the time. To put it paradoxically, the hypothesis that the atomic number expressed the intra-atomic charge could be proposed precisely because there existed no atomic number at all.

The periodic system which van den Broek proposed in 1913 is, to our eyes, quite arbitrary one and would not bear close examination. The van den Broek hypothesis proposed on such a weak foundation, however, soon came off his periodic system and began to walk independently. On the one hand, within a year it caused him to alter the meaning of his central concept, the atomic number, and on the other hand, it gave strong impact on works of Bohr, Moseley, and Soddy.

By the end of 1913, the central concept in van den Broek's argument had underwent a radical change. His hypothesis at first was concerned with the ordinal number in his new periodic system. In the letter to *Nature*, November 27, 1913,³¹ however, he used the number in the current periodic system to formulate his hypothesis. This change was caused by the result of Geiger-Marsden's 1913 experiment on the α -particle scattering. His attention was drawn to the fact that their conclusion had been obtained with a possible error which would amount to 20%. He also noticed that the ordinal number of uranium in Mendeleev's system was far smaller than half its atomic weight. Then, if Geiger-Marsden's conclusion was right, argued van den Broek, the number of elements in Mendeleev's system would be wrong, or if, on the contrary, Mendeleev's system was right, then the intra-atomic charges of heavy elements should be smaller than the value inferred from their experiment. To decide between these two possibilities, he took up the relation between the number of scattered α -particles and the nuclear charge. According to Rutherford's formula, the number of particles scattered into a given direction is expected to be proportional to the square of the nuclear charge. Although Geiger and Marsden concluded that the number of scattered particles was proportional to the square of the atomic weight, close examination of their result reveals that the proportionality is not rigorous, there being a systematic deviation from Cu to Au. But if Mendeleev's atomic number is substituted for the atomic weight, almost exact proportionality is obtained. Thus van den Broek concluded that the nuclear charge was not half the atomic weight, but equal to the atomic number in Mendeleev's system.

It should here be noted that, throughout his argument, he firmly retained the conception that the ordinal number of element in one or another periodic system

³¹ A. van den Broek, "Intra-atomic Charge," *Nature*, **92**, 372-373 (Nov. 27, 1913).

should correspond to some intra-atomic charge of the element. This conception originally was derived from the periodic systems which he composed on the principle that all the even number represented a possible element. But he now is prepared to discard those systems. Nonetheless he still regards the conception itself as valid. It operates here independently of the periodic systems from which it has emerged. We however ought not be in a hurry to conclude that he would have also discarded the notion that half the atomic weight represented the intra-atomic charge. In fact he retained this notion too. He thought that half the atomic weight would represent the total number of electrons in the whole atom, both around and inside the nucleus.

Toward the end of the letter to *Nature* considered above, van den Broek stated that since, if the mass of the atom consisted for by far the greatest part of α -particles, the total charge of the nucleus should be far greater than the value determined in the way described above, the nucleus too had to contain electrons to compensate this extra charge. In his next letter to *Nature*,³² he supposed that M (the atomic number in Mendeleev's system) was the number of electrons which constituted the negative intra-atomic charge, *i.e.* the negative charge around the nucleus, whereas half the atomic weight $A/2$ was the total number of electrons per atom. He also repeated in a letter to *Naturwissenschaften*³³ that to the continuous series of even numbers through 238 corresponded all the possible intra-atomic charges. The discrepancy between the total intra-atomic charge and the nuclear charge seemed to him to suggest the possibility of "intra-atomic isomery (different numbers of electrons with equal nuclear charge, or equal number of electrons with different nuclear charges)."³⁴

Any way, it may here be stressed that he was the first to state that the nucleus too would contain electrons, the notion which, as we shall see in the next section, was endorsed by Soddy and was generally accepted until the discovery of the neutron in 1932. It may also be added that Whittaker's account of the origin of the van den Broek hypothesis cited earlier is based solely on the letter to *Nature*, November 27, 1913. Actually van den Broek proposed a year earlier the conception that the atomic number was equal to the intra-atomic charge. The result of Geiger-Marsden's experiment motivated him to alter the meaning of the atomic number, but not to propose that conception itself.

5. Reaction

In the part II of his renowned trilogy,³⁵ Bohr begins discussion of the structure

³² A. van den Broek, "Intra-atomic Charge and the Structure of the Atom," *Nature*, 92, 476-478 (Dec. 25, 1913).

³³ A. van den Broek, "Zu dem 'Nachtrag zu dem Aufsatz von Dr. K. Fajans: Die Radioelemente und das periodische System,'" *Naturwissenschaften*, 2, 717 (July 17, 1914).

³⁴ *Ibid.*

³⁵ N. Bohr, "On the Constitution of Atoms and Molecules. Part II. Systems Containing only a Single Nucleus," *Phil. Mag.* (6), 26, 476-502 (Sept. 1913).

of general atom with citation of van den Broek's paper of early 1913 published on *Physikalische Zeitschrift*. When interviewed in the autumn of 1962 by the History of Quantum Physics project, Bohr, while speaking of van den Broek's paper as curious and without sense, admitted that his assertion concerning the number of electrons of hydrogen, helium and so on had got at the truth.³⁶ On February 5, 1913, just before his theory of the atomic structure got its final shape, he wrote to his friend C. W. Oseen a letter, in which citing van den Broek's paper of early 1913 Bohr said that his paper had to be finished quickly because other people were pursuing similar problem.³⁷ This episode tells us how deeply van den Broek's work impressed Bohr.

From the end of 1913 through 1914, around van den Broek's hypothesis arose much active discussions, especially in Britain. Its relation to the Bohr theory was often discussed. Of the earliest reactions Moseley's shall first be considered.

From his famous investigation of the characteristic X-rays, Moseley obtained the result that the quantity

$$Q = \sqrt{\frac{\nu}{(4/3)\nu_0}}$$

increased by one as he went from one element to the next in the periodic system.³⁸ In this expression ν is the frequency of K_α -line, $\nu_0 = cR$, R being the Rydberg constant. From this result he concluded that to each chemical element should correspond a quantity N which regularly increased from one element to the next on the periodic table. He says that this result proves "that there is in the atom a fundamental quantity, which increases by regular steps as we pass from one element to the next." Now such a "quantity can only be the charge on the central positive nucleus, of the existence of which we clearly have definite proof." In view of the number of electrons being roughly equal to $A/2$, we are led to "the view that N is the same as the number of the place occupied by the element in the periodic system. . . . This theory was originated by Broek and since used by Bohr."³⁹ A month or so later, Moseley, in a letter to *Nature*, manifestly stated that his "work was undertaken for the express purpose of testing Broek's hypothesis, . . . and the result of the test certainly confirms the hypothesis."⁴⁰

F. Soddy was another important figure who was enthusiastic for van den Broek's hypothesis. He was particularly interested in van den Broek's speculation stated in his letter to the 27 November, 1913 *Nature*, that there might exist electrons within

³⁶ Interview with Bohr by the History of Quantum Physics project, Session 1, Oct. 31, 1962; Session 3, Nov. 7, 1962.

³⁷ Sources for History of Quantum Physics, Bohr Scientific Correspondence 5.4.

³⁸ H. G. J. Moseley, "The High Frequency Spectra of the Elements," *Phil. Mag.* (6), 26, 1024-1034 (Dec. 1913). On Moseley's work, see John L. Heilbron, "The Work of H. G. J. Moseley," *Isis*, 57, 336-364 (1966), and P. M. Heimann, "Moseley's Interpretation of X-ray Spectra," *Centaurus*, 12, 261-274 (1968).

³⁹ H. G. J. Moseley, *Ibid.*, p. 1031.

⁴⁰ H. G. J. Moseley, "Atomic Models and X-Ray Spectra," *Nature*, 92, 554 (Jan. 15, 1914).

the nucleus too. At seeing this letter he immediately sent a letter of his own to *Nature* where he declared: "That the intra-atomic charge of an element is determined by its place in the periodic table rather than by its atomic weight, as concluded by A. van den Broek, is strongly supported by the recent generalisation as to the radio-elements and the periodic law."⁴¹ He at the same time, however, remarked that van den Broek's idea was confirmed only with regard to the relative value of the nuclear charge. He thought that there remained some uncertainty about the absolute value, because the number of rare earth elements was still uncertain.

What occupied much more space in Soddy's letter than the above was the problem of intra-nuclear electrons. He argued: On the ground of his conception of isotope, when a β -particle is emitted from within the nucleus, chemical properties of the element ought to be changed by this, whereas if the β -particles comes from extra-nuclear region of the atom, they would not change. Now recent investigation by his assistant A. Fleck has shown for uranium and thorium that the former is the case. The β -rays, therefore, are emitted from within the nucleus and, consequently, van den Broek's conception is correct. "This has resulted in a great clarification of my ideas"⁴² of isotope. Three weeks later, in a letter to *Nature*,⁴³ van den Broek agreed to Soddy's remark that there remained uncertainty about the absolute value of the nuclear charge. At the same time he tried to account for, by considering the inner structure of the atom, the fact that the characteristic X-rays was determined by the atomic number. In a paper published on the March 1914 issue of *Philosophical Magazine*, he explained in further detail the reason why he believed that electrons were contained within the nucleus.⁴⁴ His point was that the difference of the nuclear charges of uranium and lead, though smaller than the total charge to be carried away by α -particles through the whole uranium series, could be precisely explained out if the reversed change of electric charge by emission of β -particle was taken into account.

Those who discussed van den Broek's hypothesis in relation to the Bohr theory were F. A. Lindemann and J. W. Nicholson. Lindemann objected to Moseley's interpretation of his experimental results by the Bohr theory.⁴⁵ He showed that, by means of dimensional analysis, various relations between the frequency of radiation emitted by the atom and the nuclear charge could be obtained. Though there were several possible solutions, to all of them was common the fact that the nuclear

⁴¹ F. Soddy, "Intra-atomic Charge," *Nature*, **92**, 399-400 (Dec. 4, 1913).

⁴² *Ibid.*, p. 400. In 1922 Soddy again emphasized the importance of van den Broek's conception: "So far as I was concerned, this interpretation of isotopes, in the light of van den Broek's conception and Rutherford's nuclear atom, resulted in a great clarification of my own ideas," *Nobel Lectures. Chemistry 1901-1921*, pp. 393-4.

⁴³ A. van den Broek, *op. cit.* (32).

⁴⁴ A. van den Broek, "On Nuclear Electrons," *Phil. Mag.* (6), **27**, 455-457 (March 1914).

⁴⁵ F. A. Lindemann, "Atomic Models and X-Ray Spectra," *Nature*, **92**, 500-501 (Jan. 1, 1914). Full account is given in F. A. Lindemann, "Über die Grundlagen der Atommodelle," *Verh. Deutsch. Phys. Ges.*, **16**, 281-294 (1914).

charge corresponded to the place of the element in the periodic system. Thus he asserted that the Bohr theory could not necessarily be said to be proved by Moseley's result, whereas van den Broek's hypothesis was supported by it. Both Bohr and Moseley responded to this.⁴⁶ Bohr simply stated that Lindemann's dimensional analysis could not be justified. Moseley claimed that from his experiment could be derived a number of conclusions which supported the characteristic features of the Bohr theory. He also stated, as we have already seen, that his experiment had been carried out with the purpose of testing van den Broek's hypothesis. Neither of them did not enter further detail

Nicholson examined the mechanical stability of the electron rings of the Bohr atom.⁴⁷ This examination led him to suggest that van den Broek's hypothesis would not hold good for lithium, beryllium, and boron. If, according to Bohr, all the electrons are assumed to have the equal angular momentum $h/2\pi$, a system with three electrons on two concentric rings, which was adopted by Bohr as the model for the lithium atom, would be unstable. A three electron system is stable only when all the electrons are distributed on one and the same ring. Either the Bohr theory or the van den Broek hypothesis should therefore be abandoned. Thus Nicholson concluded that perhaps the latter was to be abandoned, at least for Li, Be, and B. Van den Broek refused this conclusion.⁴⁸ He argued that his hypothesis was, for the elements from hydrogen to carbon, simply an expression of experimental fact, and was most strongly supported by Moseley's second paper on the characteristic X-rays.⁴⁹ Confronted with this objection Nicholson shifted his position.⁵⁰ He now accepted the van den Broek hypothesis and denied the Bohr theory. He, on the one hand, admitted that Moseley's result supported the hypothesis, but on the other hand asserted that the Bohr theory would not give correct formula for helium spectrum.

The problems raised by both Lindemann and Nicholson were by no means of such a kind as to motivate or to give moment to the subsequent development of atomic physics. They did neither imply problem which bore any importance for the future development of the Bohr theory, nor disclosed some aspect of the sharp break of it with the classical theory. They therefore would not be of much historical

⁴⁶ N. Bohr, "Atomic Models and X-Ray Spectra," *Nature*, **92**, 553-554 (Jan. 15, 1914). H. G. J. Moseley, *op. cit.* (40).

⁴⁷ J. W. Nicholson, "Atomic Models and X-Ray Spectra," *Nature*, **92**, 583-584 (Jan. 22, 1914). Beside this, Nicholson wrote a few papers examining the validity of the Bohr Theory: "Atomic Models and X-Ray Spectra," *Nature* **92**, 630 (Feb. 5, 1914); "The High-frequency Spectra of the Elements, and the Structure of the Atom," *Phil. Mag.* (6), **27**, 541-564 (April 1914); "Atomic Structure and the Spectrum of Helium," *Phil. Mag.* (6), **28**, 90-103 (July 1914).

⁴⁸ A. van den Broek, "The Structure of Atoms and Molecules," *Nature*, **93**, 241-242 (May 7, 1914).

⁴⁹ H. G. J. Moseley, "The High-frequency Spectra of the Elements. Part II," *Phil. Mag.* (6), **27**, 703-713 (April 1914).

⁵⁰ J. W. Nicholson, "The Constitution of Atoms and Molecules," *Nature*, **93**, 268-269 (May, 14, 1914).

interest. But they at least furnish examples of the attitude of those who were doubtful about the Bohr theory and yet favourable to the van den Broek hypothesis. This seems to reinforce our suggestion that the van den Broek hypothesis was received almost unanimously as a very natural proposition.

Van den Broek wrote further two short notes in order to strengthen his hypothesis.⁵¹ In both of them he stressed that the spectra of characteristic X-rays were best expressed in terms of the atomic number. After this he apparently wrote no paper which was directly concerned with the atomic number hypothesis.

6. Speculation on the Structure of the Atom

Before concluding this paper, a few words may also be devoted to another aspect of van den Broek's speculation, which proves to be very interesting in view of the later development of the atomic physics.

Considerable part of the 1913 paper,⁵² in which van den Broek first stated the atomic number hypothesis, was devoted to consideration of the arrangement of electrons around the nucleus. There he predicted the shell structure of electrons. The first ground for supposing the shell structure was furnished by the analysis by Rutherford of the energy spectrum of γ -rays from RaC.⁵³ Rutherford obtained the conclusion that the energy of the γ -rays from RaC could be expressed by a formula $E_0 - (pE_1 + qE_2)$, where E_0 was the maximum value of the energy, and p and q were integral numbers. He interpreted this formula as follows. Inside the atom there would be two distinct regions 1 and 2 where an electron, passing through each of them, is slowed down to radiate γ -rays. If we denote the energy lost by electron passing through each of the regions by E_1 and E_2 respectively, and assume that when the electron passes through the regions 1 and 2, it radiates p and q γ -rays respectively, the total energy radiated out will be $pE_1 + qE_2$. Here Rutherford did not use the term "quanta" of radiation. Now if we further assume that all the γ -rays are originally emitted with equal energy E_0 , the formula above will immediately follow. Rutherford also observed small number of γ -rays which largely deviated from the preceding formula. Upon this observation he suspected the third region in which generation of γ -rays would require much more energy than in the first or second region. It should be remembered that at this time he considered β -rays to be excited electrons ejected out from the region outside the nucleus.

The second ground that van den Broek adduced in favour of the shell structure was J. J. Thomson's experiment on canal rays of 1912 which showed that mercury atom could be ionized to $+8$.⁵⁴ Since obviously the valence of mercury is not eight, argued van den Broek, this result must indicate that there is a group of electrons

⁵¹ A. van den Broek, "Ordinals or Atomic Numbers?" *Phil. Mag.* (6), 28, 630-632 (Oct. 1914); "Röntgenstrahlung und Ordnungszahlen," *Phys. Zeits.*, 15, 894-895 (Nov. 1, 1914).

⁵² *Op. cit.* (3), pp. 38-40.

⁵³ E. Rutherford, "The Origin of Beta and Gamma Rays from Radioactive Substances," *Phil. Mag.* (6), 24, 453-462 (Oct. 1912).

⁵⁴ J. J. Thomson, "Multiply-charged Atoms," *Phil. Mag.* (6), 24, 668-672 (Oct. 1912).

other than those responsible for valence. The third ground cited by him was the behaviour of the characteristic X-rays. J. J. Thomson considered the characteristic X-rays as originating from a group of electrons which were much more firmly bound together than those responsible for ionization.⁵⁵ Combining this interpretation with the fact that as the atomic weight increased there appeared successively three series of X-ray lines, K, L, and M, van den Broek supposed that there would be at least three distinct groups of electrons from which the characteristic X-rays originated.

Resuming these considerations he concluded that the atom probably contained, according to its atomic weight, one to five distinct groups of electrons. They are, from the outermost inward, the one which determines the valence, Thomson's octet group, and those 3 groups responsible for the characteristic X-rays, the existence of which had also been inferred from Rutherford's analysis of γ -rays emitted from RaC. Such a shell structure was also favourable to the periodic system proposed by van den Broek. In his periodic system there were many places which were occupied by more than one element. Chemical properties of those elements naturally ought to be similar to each other. This similarity would easily be accounted for if one assumes that as the atomic number increases, additional electrons join an inner group of electrons, the group of valence electrons being unaltered. More than this, remarked van den Broek, according to Thomson's theory of the atomic structure, new electron ring should be formed successively in the inner part of the atom as the number of electrons increases. With regard to the positive charge within the atom, however, Thomson's model cannot be accepted. But since, according to Rutherford, the positive charge is confined within an extremely small region, the structure of the positive charge would do little with the properties of the atom. This again confirms, concluded van den Broek emphasizing his hypothesis, that it is the number of electrons that bears fundamental importance for the properties of the atom.

His consideration outlined above draws much our interest. It may be said that, before Bohr introduced the concept of energy level, van den Broek obtained in advance, anticipating the shell structure of extra-nuclear electrons, some conceptions which were to be established later. It is also interesting to note how great and influential were J. J. Thomson's contributions to the inquiry into the atomic structure although his model itself eventually proved to be incorrect.

There naturally arises the question whether and, if any, how van den Broek's insight into the shell structure was subsequently developed by others. To say the conclusion, it attracted little attention of others. Van den Broek himself, after the early 1913 paper, again considered the arrangement of intra-atomic electrons in the letters to 25 December issue, 5 March issue, and 11 June issue of *Nature*.⁵⁶

⁵⁵ J. J. Thomson, "Ionization by Moving Electrified Particles," *Phil. Mag.* (6), 23, 449-457 (April 1912), esp. pp. 456-7.

⁵⁶ A. van den Broek, *op. cit.* (32), "Atomic Models and Regions of Intra-atomic Electrons," *Nature*, 93, 7-8 (March 5, 1914); and " α - and β -Rays and the Structure of the Atom (Internal-Charge Numbers)," *Nature*, 93, 376-377 (June 11, 1914).

The arguments developed there were essentially the same as outlined above. No evidence which indicates that someone took interest in his insight has thus far been found. Only toward the end of 1915, W. Kossel⁵⁷ in the introduction of his paper dealing with the arrangement of extra-nuclear electrons on the basis of chemical consideration, cited van den Broek as well as Bohr as the pioneers attempting to account for the chemical properties of the atom on the basis of its inner electronic structure.

7. Concluding Remark

Van den Broek's hypothesis was a product of his continuing effort to establish mutual relations of chemical elements.

His hypothesis originated, as we have seen above, in his trials of constructing a comprehensive periodic system. The periodic system of element was generally intended to establish the natural order which would bring chemical elements into connection with each other. Interest in mutual relations of elements seems to have continued to be the most basic and strongest drive for the scientific speculation of van den Broek's. For example, in 1914 he published a paper which was intended to establish a relation between the half-value periods of the corresponding radioactive products of three radioactive series.⁵⁸ By the corresponding products he meant those products belonging to different radioactive series which had the same atomic number. Denoting the half-value periods of corresponding products of thorium, radium, and actinium series by Th_T , Ra_T and Ac_T respectively, he asserted that there was the relation

$$Th_T = \sqrt{Ra_T Ac_T / c^{M-M(Pb)}}$$

where M is the atomic number of the products in question, $M(Pb)$ that of lead, and $c = \text{const.} = \pm 4.5$. No theoretical foundation of this formula was stated. It merely expressed a relation which was contingently satisfied by observed values of those quantities. F. A. Lindemann, however, regarded this formula as indicating the importance of the nuclear charge. He therefore tried to give it a theoretical foundation.⁵⁹

In 1916 van den Broek tried to establish, on the analogy with radioactive series, a scheme which was to predict the distribution of isotopes of light elements.⁶⁰ In the same year he also tried to find a scheme which would represent families of twin or doubly twin elements in the periodic system.⁶¹ By twin element he meant those

⁵⁷ W. Kossel, "Über Molekülbildung als Frage des Atombaus," *Ann. d. Phys.* (4), 49, 229-362 (1916), esp. p. 229.

⁵⁸ A. van den Broek, "Radio-activity and Atomic Numbers," *Nature*, 93, 480 (July 9, 1914).

⁵⁹ F. A. Lindemann, "Radio-activity and Atomic Numbers," *Nature*, 93, 584 (Aug. 6, 1914).

⁶⁰ A. van den Broek, "Über die Isotopen sämtlicher chemischen Elemente," *Phys. Zeits.*, 17, 260-262 (June 15, 1916).

⁶¹ A. van den Broek, "Eine allgemeine Zwillingsreihe der Atomarten," *Phys. Zeits.*, 17, 579-581 (Dec. 1, 1916).

elements which were connected by the emission of α -particle, or a pair of two elements, one with an odd atomic number and an atomic weight $4n$ and the other with an even atomic number and an atomic weight $4n + 3$.

These attempts can not be said of any scientific significance. They are indeed amateurish attempt lacking sound foundation. But they at the same time reveal the characteristic feature of van den Broek's way of investigation. He always paid attention to latest scientific informations of various kinds. His interest lay in establishing an often superficial relation among them. He usually did not pay due attention to both whether it has physical foundation or necessity, and whether there is consistency among his various attempts. Such an attitude in many cases made his venture merely an *ad hoc* idea. At the same time, however, it made for him sometimes possible to propound an audacious hypothesis. The atomic number hypothesis may be said the most successful case of his amateurish audacity. The hypothesis was proposed, as we have occasionally remarked, on a rather arbitrary basis. But when it was published, the time was ripe. It gave a clear expression to what the contemporary physicists were, consciously or unconsciously, at the point of grasping. Precisely for this reason, we may conclude, his hypothesis was rapidly accepted and could give considerable impact on the development of the atomic physics of the time.

Throughout this investigation I have much profited by the ample knowledge of Mrs. S. Nisio about the state of the atomic physics in those days. Mr. J. Nemoto of the Meteorological Agency has offered me much convenience in using literature at the library of the Agency. I would like to express my cordial thanks to both of them.