PERIODICITY IN THE STRUCTURE OF THE ELECTRON ENVELOPES AND NUCLEI OF ATOMS*

COMMUNICATION 1. PERIODIC SYSTEM OF THE ELEMENTS AND ITS CONNECTION WITH THE THEORY OF NUMBERS AND WITH PHYSICOCHEMICAL ANALYSIS

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1. Introduction

The fundamental law of chemistry — Mendeleev's periodic law — is manifested in a great variety of ways. It is most intimately bound up with the theory of atomic structure, and the periodic system of the elements derived from it consists in the classification of atoms according to the structures of their electron envelopes. The electronic theory of atomic structure and valency could not have developed, and cannot continue to develop, without the direct and determining participation of the Mendeleev law and the Mendeleev system. The question of the structure of the periodic system of the elements has been the subject of numerous investigations, which we have referred to in a series of communications [1,2,3]. In these communications we have considered, in a concise but sufficiently detailed fashion, the facts and principles that must find their expression in a modern scheme of the system of elements. In the present paper, in our considerations of the structure of the periodic system arrived at in this way, we shall confine ourselves to such exposition of the structure as is necessary for the comprehension of a treatment in which we throw further light on the system by the use of number theory and physicochemical analysis.

The use of mathematics as a means of generalizing data obtained by experiment, which is so characteristic of modern chemistry, does not replace real physicochemical objects by fictitious, abstract mathematical concepts. The object in our inferences here, and in other fields of science (for example, that of the phase rule) which are concerned with definite numerical relationships, is to represent facts observed by chemists by means of geometric models, and also to describe them with the aid of the language of mathematics. It is quite obvious that the systematization and description of known facts with the aid of mathematical terms and method cannot and does not lead to anything more than that which experiment yields to the investigator.

2. Structure of the Periodic System of the Elements

The rational structure of the periodic system of the elements contains: a) a zero period and zero group of elements; b) a subdivision of the system into even and odd periods and into cycles, which express a secondary periodicity; c) an evolutionary representation of the nature of the elements (proto-elements → typical elements → elements "of complete structure"). In Fig. 1 a stepwise representation of the system is given; in this the black spots represent elements of the even periods and circles represent those of the odd periods. The numbers of elements in the periods and in the cycles, each of which consists of a pair formed by an even and an odd period, are given below the diagram. The system is complete up to centium (z = 100). The same can be expressed by means of a network of cells (Fig. 2). The bold line represents a discontinuity; the cell occupied by hydrogen rests simultaneously on cells of groups I and VII. In the left part of the diagram the periods and cycles are given; and below the actinides and lanthanides are shown. The detailed derivation of these representations of the system, as also the arguments relating to the necessity of introducing the electron (e) and the neutron (n) into the system, is not given here (see [3]). We will add that in the table in Fig. 2 atomic weights are given and the recently discovered elements Athenium (An) and Centium (Ct) are included (as also in Fig. 1. The 6d shell is completed at element 104**.

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** Seaborg proposes to call it ekahafnium [4].

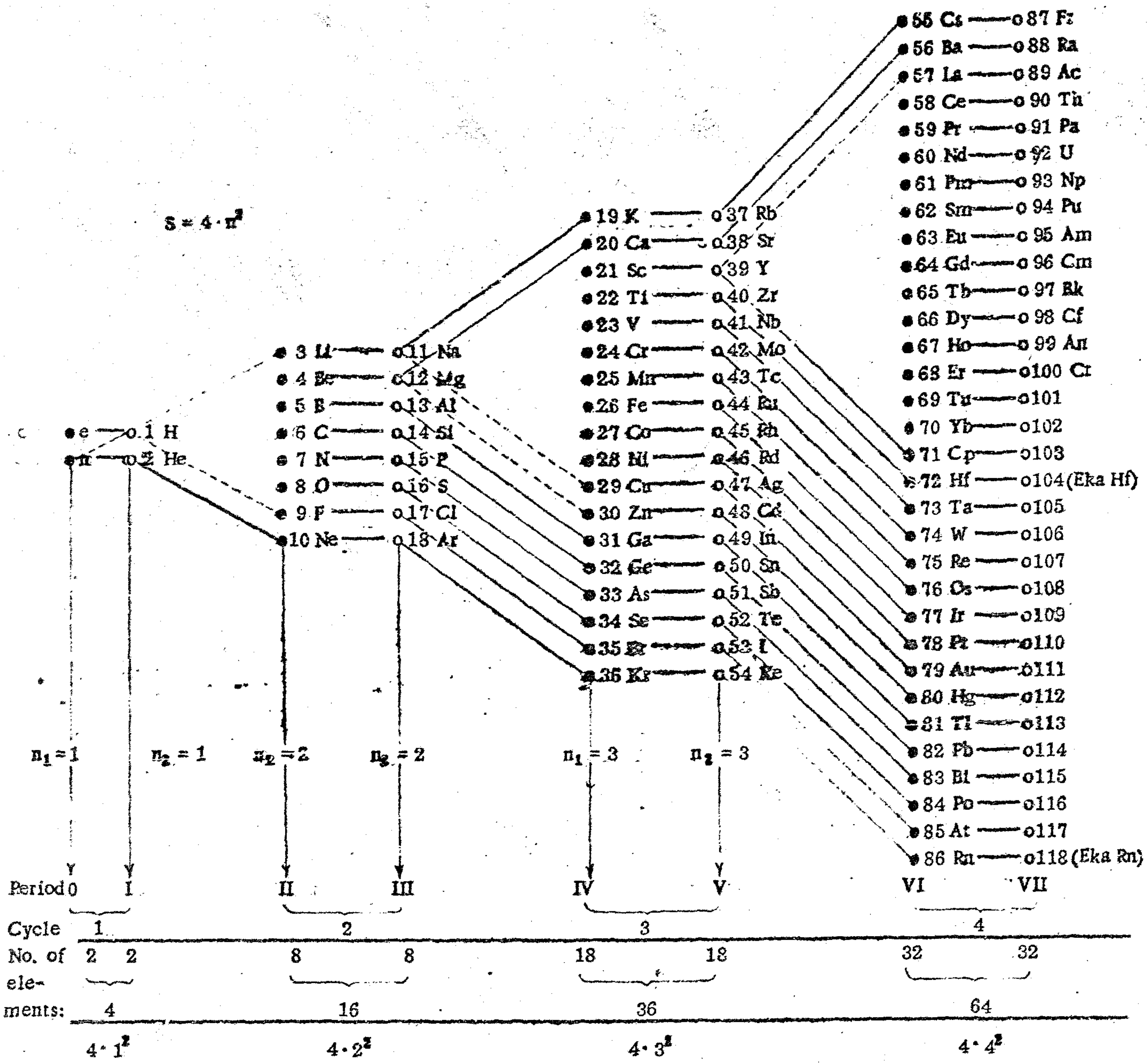

Fig. 1. Stepwise representation of the system

and at the end of the system is an atom of the inert-gas type belonging to the zero group, which it would be correct to call ekaradon (EkaRn). Altogether, there are 18 elements that have still not been discovered: from centium (100) to ekaradon (118). There can be no doubt that in their preparation, as also in their investigation, Mendeleev's law will play the same leading part as it has played up to the present.

3. Periodicity of the Properties of the Elements, and the Theory of Numbers

There can be no doubt that it is in the theory of numbers that we find the best way of describing the periodic law and the periodic system in mathematical terms, for this branch of mathematics concerns itself with discontinuous quantities. Although Mendeleev pointed this out more than half a century ago [5], there have been no systematic attempts to apply the theory of numbers in chemistry.

D. I. MENDELEEV'S PERIODIC SYSTEM OF THE ELEMENTS

Cycle	Period	Series	Group 1	2	3	4	5	6	7	8			0
1	0	0	0 e										0 n 1.008
	1	1	1 H 1.008										2 He 4.003
2	2	II	3 Li 6.94	4 Be 9.013	5 B 10.82	6 C 12.010	7 N 14.008	8 O 16.000	9 F 19.00				10 Ne 20.183
	3	III	11 Na 22.997	12 Mg 24.32	13 Al 26.97	14 Si 28.06	15 P 30.98	16 S 32.066	17 Cl 35.457				18 Ar 39.944
3	4	IV	19 K 39.096	20 Ca 40.08	21 Sc 45.10	22 Ti 47.90	23 V 50.95	24 Cr 52.01	25 Mn 54.93	26 Fe 55.85	27 Co 58.94	28 Ni 58.69	
		V	29 Cu 63.57	30 Zn 65.38	31 Ga 69.72	32 Ge 72.6	33 As 74.91	34 Se 78.96	35 Br 79.916				36 Kr 83.7
	5	VI	37 Rb 85.48	38 Sr 87.63	39 Y 88.92	40 Zr 91.22	41 Nb 92.91	42 Mo 95.95	43 Tc [99]	44 Ru 101.7	45 Rh 102.91	46 Pd 106.7	
		VII	47 Ag 107.88	48 Cd 112.41	49 In 114.76	50 Sn 118.70	51 Sb 121.76	52 Te 127.61	53 I 126.92				54 Xe 131.3
4	6	VIII	55 Cs 132.91	56 Ba 137.36	57 La *	72 Hf 178.6	73 Ta 180.88	74 W 183.92	75 Re 186.31	76 Os 190.2	77 Ir 193.1	78 Pt 195.23	
		IX	79 Au 197.2	80 Hg 200.61	81 Tl 204.39	82 Pb 207.21	83 Bi 209.00	84 Po [210]	85 At [211]				86 Rn 222
	7	X	87 Fr 223	88 Ra 226.05	89 Ac * *								
		XI	—	—	—	—	—	—	—				118 Eka Rn

LANTHANIDES

57 La 138.92	58 Ce 140.13	59 Pr 140.92	60 Nd 144.27	61 Pm 147	62 Sm 150.43	63 Eu 152.0	64 Gd 156.9	65 Tb 159.2	66 Dy 162.46	67 Ho 164.9	68 Er 167.2	69 Tm 169.4	70 Yb 173.04	71 Lu 174.99

ACTINIDES

89 Ac 227	90 Th 232.12	91 Pa 231	92 U 238.07	93 Np 237	94 Pu [239]	95 Am [241]	96 Cm [242]	97 Bk	98 Cf	99 An	100 Ct	101	102	103

*Lanthanides * *Actinides

Fig. 2.

The use of mathematics in chemistry is possible on account of the correlation principle, which establishes the correspondence of mathematical forms and their transformations with physicochemical objects and the changes that they undergo. Therefore, we shall first establish corresponding chemical and mathematical concepts for examination. Kurnakov [6], in writing that "the law of constant and multiple proportions is an application of the study of whole numbers to chemistry", shared the views of Kummer [7], according to whom "chemistry and the theory of numbers have as their principle — although in different spheres of activity — the same concept of composition". Composition in chemistry is expressed with the aid of the concept of element, and an element is a form of material to which a definite place in Mendeleev's system corresponds. This definition is in complete accord with that proposed by Kedrov [8]: "an element is a species of atoms that occupy one definite place in Mendeleev's system".

In the system, the cell, which is denoted by a serial number (the atomic or Mendeleev number), is the element's "passport", characterizing its individual nature. Thus, to the number concept in mathematics there is a corresponding concept in chemistry of atomic, or cell number.

Among all the kinds of periodic relationships in chemistry, the most perfect and all-embracing is the system of elements. Can there be among the various mathematical functions one that could express the extremely high degree of organization and interrelationship of discontinuous quantities; that would have a dual character, expressing in itself the interaction of these quantities and the unity of their opposing characteristics; that would be constructed on the basis of the periodicity concept, not in the sense of simple repetitivity, but a concept of periodicity in its evolution at ever higher and higher levels, although in the form of an abstraction — a form that expresses in itself the transition from quantity to quality — a function that itself determines the composition of the groupings that arise ?

Number theory enables us to give an answer to this question. Let us suppose that we have the natural series of integers from 1 to 120 (the basis for the upper limit will be given later):

$$1,\ 2,\ 3,\ 4,\ 5,\ 6,\ 7,\ 8,\ 9 \ldots\ldots\ldots\ldots\ldots 120.$$

In this series particular sets of numbers show various forms of periodicity, as may be seen, for example, for the Bernoulli numbers; the repetitivity may vary greatly. Which of the possible solutions corresponds to the criteria given above? We may first of all eliminate the variant of simple mechanical repetition, for the main requirement is the possibility of repetition that includes in itself evolution, i.e., that continually passes to a higher and higher level. This requirement corresponds to the next in order of reducing simplicity after the natural series: the series of squares of even numbers, 2^2, 4^2, 6^2, 8^2..., i.e., 4, 16, 36, 64,... We then have a periodicity of defined number cycles, which grow regularly as we move from the beginning of the series, thus satisfying the requirement given above.

The solution would remain incomplete if the concept of composition, so important from the chemist's point of view, were not expressed in it. According to the theory of numbers [9], every integer has at least two factors: itself and unity. A number having only two factors is prime, and one having more factors is composite. In the natural series of numbers 4 is the first and simplest composite number. Hence, the question of the composition of groupings of numbers developing cyclically in the natural series is equivalent to the question of repetitivity, in conformity with rule, of the simplest composite number, i.e., four, both as a beginning and as a basis. It has a simple and unequivocal solution, for the sets of numbers given above consist in an n^2-times repetition of four. In fact, every one of them is expressed by the formula $4 \cdot n^2$, where $\underline{n}$ is the number of the given grouping obtained by counting in order from the beginning of the system. Thus, the series of natural numbers contains growing cycles, each having $\underline{S}$ members and conforming to an extremely simple expression, which is not equivalent to other axioms, or theorems, and which is intimately bound up with the mathematical concept of composition, namely:

$$S = 4 \cdot n^2 .$$

By giving $\underline{n}$ the values 1, 2, 3, 4 we find that $\underline{S}$ becomes 4, 16, 36, 64. This expression is symmetrical and is in accord with the criterion of evenness and, in fact, duality.

The symmetry can be expressed by the condition stating that if the basis of the system is four, then its number of terms is also four. We then obtain a system of numbers:

$$4 \cdot 1^2 + 4 \cdot 2^2 + 4 \cdot 3^2 + 4 \cdot 4^2 = 120.$$

The evenness and dual character of this system permit us to break down each cycle into two halves. We have an analogous picture in a wave, which is composed of two half-waves. We shall call them number periods. According to definition, the number of numbers in the periods (which combine in pairs into cycles) will be (in order):

$$2,\ 2,\ 8,\ 8,\ 18,\ 18,\ 32,\ 32.$$

The system under consideration, therefore, forms itself into two number "rays" of periods — even and odd (according to the serial number of the period). Let us consider the results so obtained. With the aid of the theory of numbers and by an examination of the regularities found in the series of integers 1, 2, 3, 4, 5, 6 ......120, we conclude that within the limits of such a series:

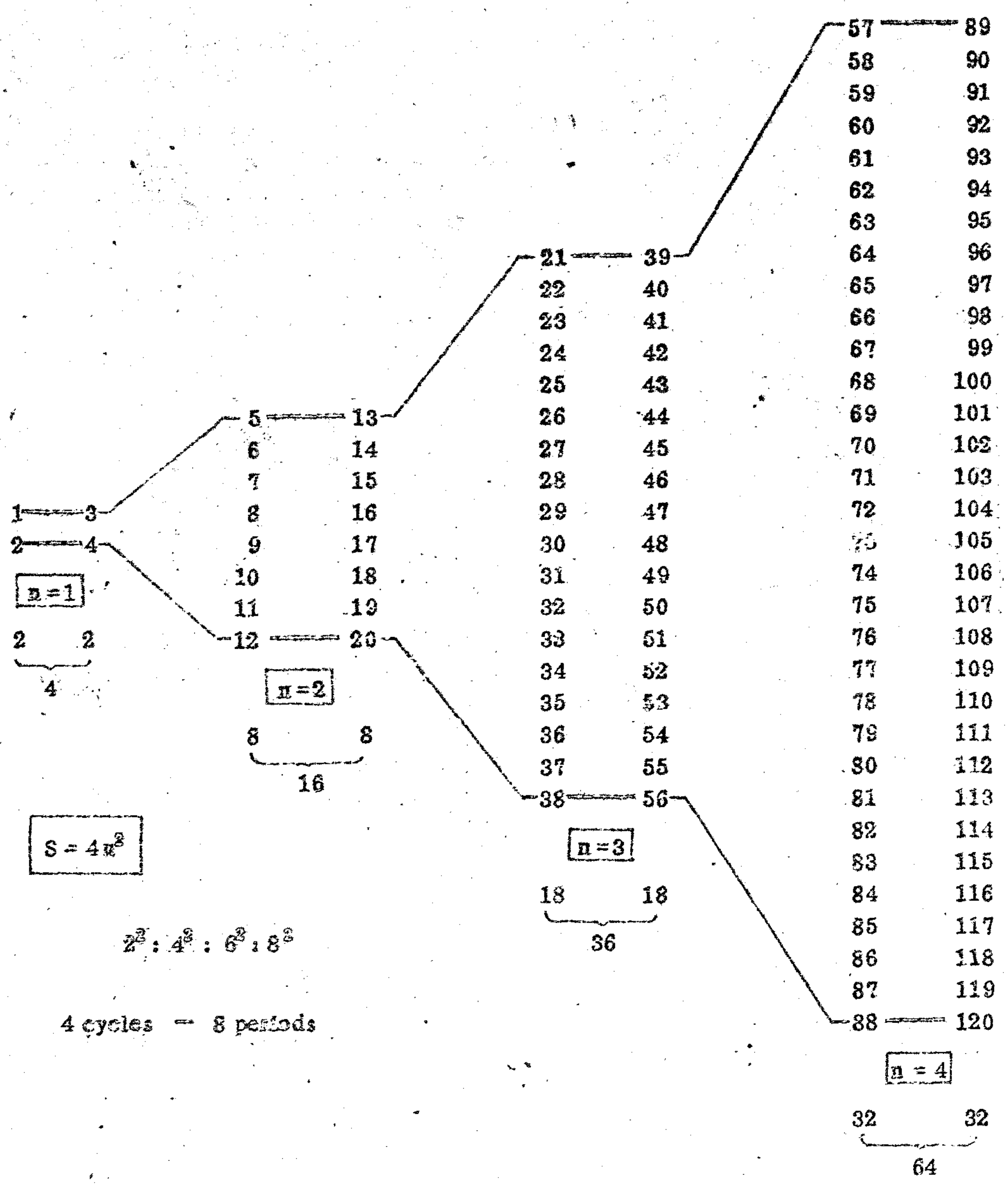

Fig. 3. Number system for n^2-times repetition of the simplest composite number.

a) there is a periodicity expressed by the set of numbers 1, 2, 3, 4, 5, 6 ......,120;

b) the periods combine in pairs, each comprising an even and an uneven period, containing groupings of 4, 16, 36, 64, which conform to the law of an n^2-times repetition of the simplest composite number.

Such a mathematically derived concept of periodicity includes not only repetitivity of definite groupings (n^2-times repetition of the simplest composite number, four), but also the growth of cycles as they evolve; it expresses also the dual character and symmetry of structure of the system of numbers obtained — a structure formed by two — even and uneven — rays of periods. It is not difficult to see that we have satisfied all the requirements of a mathematical representation of the periodic system of the elements, the starting point for which is the correspondence between the concept of element in chemistry and that of number in mathematics, as formulated by us at the beginning. There only remains the final step of constructing a series of numbers from 1 to 120 following the results of the mathematical analysis of periodicity obtained above (Fig. 3).

A comparison of Figs. 1 and 3 confirms the complete identity of the periodic system of numbers with the variant we have developed of Mendeleev's periodic system. The structures of the two systems are identical. All parts of the two systems, in agreement with the correlation principle, correspond with one another: a) number —

element; b) "half-wave" or number period — period of the system of elements; c) number cycle — cycle of the system of elements, which combines within itself an even and an odd period.

It is obvious, of course, as we emphasized at the very beginning, that we have here a correspondence, not an identity. There is no simple equality between a mathematical number and a Mendeleev number. The former gives a formal ordinal number in the system, and the latter, in as much as the first two elements, the electron and neutron, have zero Mendeleev numbers, is equal to the nuclear charge. However, even the electron and the neutron, being individuals, correspond in the mathematical system to numbers (1 and 2). For this reason there is a displacement by two places in the succession of "chemical" numbers in comparison with the "mathematical" numbers, a circumstance that is without fundamental or practical significance for the mathematical expression of the periodic system of elements. What, then, is the physical meaning of the numbers that run like a red thread through the system under consideration, i.e., 2 and 4?

First of all, it will be noted that 2 is the two possible values of the spin, and 4 is the four quantum numbers s, p, d, and f. But the most general and therefore the most correct explanation is that 2 expresses the dual character of the system of elements, and the simplest composite number 4 is the number of proto-elements (electron, neutron, proton, α-particle), which lie at the basis of the system and enter into the composition of the atoms of the remaining elements. All that we have expounded here, of course, is applicable both to the evolutionary and to the cell representation of the system.

The concept of "system" is wider than that of "periodic law" in its generally accepted formulation. It is true that a mathematical analysis of its structure indicates an exact correspondence between the system and the law of the periodic dependence of properties on the place occupied by the element in the system (Mendeleev periodicity), but that is not all. It emerges very strikingly from the system that the periods themselves, being repeated in a cyclic fashion, exhibit a "periodicity of periods", or secondary periodicity, which was first discovered by Biron [10]; it is not expressed at all in Mendeleev's formulation of the law and is closely associated with the general structure of the system in accord with the results of experimental chemistry [2].

What we have given above is not a mathematical derivation of the periodic system of elements. It is impossible to derive a real physical law from abstract numbers. Also, the correspondences that we have established are in no way intended as a replacement of the periodic law, in all its variety, by simple mathematical equations; they are intended to throw light on one part, although it is a very important part, of the problems relating to the structure of the system of elements. We are concerned only with the mathematical expression of experimentally found generalizations, but this is indeed a step toward the goal of Mendeleev — the discovery of an exact expression of the periodic law and of the periodic system of elements.

4. Physicochemical Analysis and Geometry of the Structure of the Mendeleev Periodic System of Elements

Graphical representation of various physicochemical systems and processes is widely used in general and physical chemistry. It has found its widest application in Kurnakov's physicochemical analysis, which brings together chemistry and geometry on the basis of correlation principles and of the continuity of transformations, and which enables us to make a new approach to the concept of the chemical individual.

It is possible that further development of the study of singular points in composition—property diagrams will reveal new methods for the graphical interpretation of Mendeleev's periodic law, in as much as the correspondence of any individual (daltonide) to a singular point coincides with the correspondence of an element — which is a chemical individual — to the concept of a special point in geometry. At the present time, however, at least without fundamental changes in the basic principles of physicochemical analysis, it is impossible to count on success in this direction.

The reason for this is that the method of physicochemical analysis, which can be successfully extended to any composition—property diagrams whatever, is strictly based on thermodynamical principles, as Kurnakov emphasized [6]. There is good reason why the main concept with which it operates should be the concept of a phase, homogeneous and continuous, as defined by classical thermodynamics. This is closely related to the fact that the principle of continuity of transformations occupies the foremost place in the theory of physicochemical analysis. The main laws, obtained in strict fashion by the use of above-described concepts, are extended further to non-equilibrium systems and non-thermodynamical properties.

However, neither the concept of the phase nor the principle of continuity of transformations is applicable to the analysis of the periodic system of the elements. In the first place, the periodic system is a system of atoms. It relates essentially to isolated atoms and also has no specific character such as is peculiar to statistical assemblies, i.e., phases, and is therefore like any generalization relating to the structures of atoms and molecules. In the second place, at least in the available range of temperature and pressure, there are no states of equilibrium and continuous transformations between the various elements; the periodic law cannot therefore be expressed with the aid of continuous functions. Hence, the geometry of the structure of the periodic system of elements must also be the geometry of discontinuity. Here lies the essential difference from the usually applicable methods of physico-chemical analysis. In all other respects, however, the ideas upon which Kurnakov based the theory of composition–property diagrams are quite applicable to the solution of the question of the geometrical representation of the structure of the periodic system of elements.

In accord with the correspondence principle, the concept of the element in discontinuous geometrical figures has its counterpart in the elementary square or cell. The next concept in complexity, the period, corresponds to a parallelogram (rectangle): the number of cells that it contains, which is equal to its area, is the number of elements in the period. Two contiguous periods (even and odd) taken together form a single cycle of the system. Thus, the geometrical counterpart of the cycle in the system of elements is the square, which is composed of two rectangles (right and left); its symmetry is expressed in its square outline, and the number of cells that it contains, which is equal to the number of elements, is therefore determined by the quadratic expression: $S = 4n^2$, where n is the series of integers.

C = 1

	0	1
P	e_0	1 H
A	n_0	2 He

C = 2

	2		3	
P	3 Li	7 N	11 Na	15 P
A	4 Be	8 O	12 Mg	16 S
P	5 B	9 F	13 Al	17 Cl
A	6 C	10 Ne	14 Si	18 Ar

C = 3

4			5			
19 K	25 Mn	31 Ga	37 Rb	43 Tc	49 In	P
20 Ca	26 Fe	32 Ge	38 Sr	44 Ru	50 Sn	A
21 Sc	27 Co	33 As	39 Y	45 Rh	51 Sb	P
22 Ti	28 Ni	34 Se	40 Zr	46 Pd	52 Te	A
23 V	29 Cu	35 Br	41 Nb	47 Ag	53 I	P
24 Cr	30 Zn	36 Kr	42 Mo	48 Cd	54 Xe	A

Fig. 4. Representations of cycles.

Starting from this correspondence of elements and structural parts of the periodic system with discontinuous geometrical forms, we can construct the corresponding representations for each of the cycles (Figures 4 and 5). In each square the cells corresponding to the elements are disposed in the order of the Mendeleev numbers of the elements. The "anisotropy" of each square consists in the fact that even and odd numbers (Mendeleev numbers) are brought together in alternative horizontal rows, thus bringing together Shchukarev's artiads and perissads [11] (denoted by A and P). Above each square the number of the cycle (C) is given, and above each rectangle, the number of the period.

It will be seen from the number of variables under examination that the system cannot be completely represented on a plane; it can be represented only in three-dimensional space. A three-dimensional figure containing squares in the form of sections parallel to the base separated by distances proportional to the capacities of the cycles is to be found in a truncated tetragonal pyramid (Fig. 6), which has a symmetry that is characteristic of the structure of Mendeleev's periodic system of elements and which consists of two halves, related symmetrically as mirror images, which are assigned to even and odd periods, respectively.

C = 4

	6				7			
P	55 Cs	63 Eu	71 Cp	79 Au	87 Fr	95 Am	103	111
A	56 Ba	64 Gd	72 Hf	80 Hg	88 Ra	96 Cm	104	112
P	57 La	65 Tb	73 Ta	81 Tl	89 Ac	97 Bk	105	113
A	58 Ce	66 Dy	74 W	82 Pb	90 Th	98 Cf	106	114
P	59 Pr	67 Ho	75 Re	83 Bi	91 Pa	99	107	115
A	60 Nd	68 Er	76 Os	84 Po	92 U	100	108	116
P	61 Pm	69 Tu	77 Ir	85 At	93 Np	101	109	117
A	62 Sm	70 Yb	78 Pt	86 Rn	94 Pu	102	110	118

Fig. 5. Representation of a cycle.

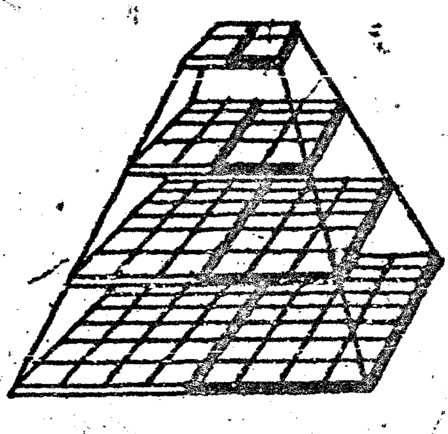

Fig. 6. Spatial representation of the system.

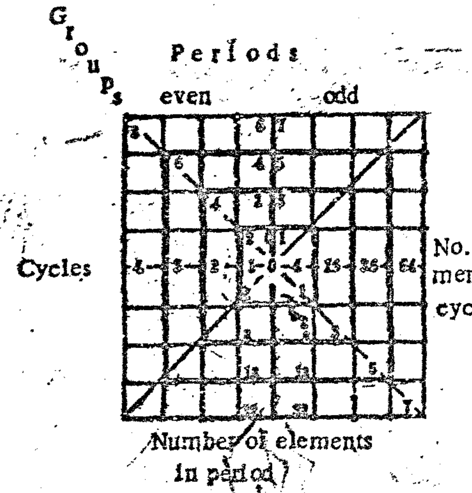

Fig. 7. Projection on the base of the spatial representation of the system.

This three-dimensional form of representation can be projected onto the base. The figure so obtained also presents a geometric expression of the structure of the periodic system of elements (Fig. 7). In the examination of this diagram, as also of the previous ones, it must be remembered that it is concerned with the geometric representation of the system and is not intended to replace in any way the evolutionary and tabular forms of the system (see Section 2).

In the geometric form given in Fig. 7, the interrelations of elements, periods, cycles, and (along the diagonal) groups are presented. The boundaries of the cycles are indicated by bold lines. All other indications are given directly on the figure. Such a diagram enables the interrelationship between all the concepts used in the construction of the periodic system to be represented in an extremely graphic fashion.

Just as, according to Kurnakov [6], any composition — property diagram is a closed complex, so in the diagram that we have advanced for the periodic system of the elements we find, using the word in the same sense, a closed diagram.

The geometric interpretation of the periodic system is in complete accord with the representation of the system in terms of number theory. "The system presents itself to us as a unified whole, harmoniously developed and having a regular and logical structure, answering in spirit and sense the designation "system"; its fundamental completeness is evident; it is incomplete only with respect to the discovery of new elements, in the effecting of which it will form, as it has done in the past, a leading thread in the investigations. All that we have expounded above will help in the realization of Mandeleev's goal: to give mathematical representations of the system with the aid of number theory and the geometry of discontinuous quantities.

SUMMARY

1. A horizontal, cell-form representation of the periodic system of elements is given in which

a) a zero period (electron, neutron) and zero group (neutron, He, Ar, Ne, Kr, Xe, Rn, ekaradon) are included;

b) subdivision is into periods and cycles expressing secondary periodicity;

c) there is a hydrogen "cell" adjoining Groups I and VII.

2. It has been shown that the structure of Mendeleev's periodic system can be described with the aid of number theory; and Kurnakov's physicochemical analysis is applied to the geometric representation of the periodic system.

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