[Contribution from the Kent Chemical Laboratory of the University of Chicago]

ISOTOPES: A NEW RELATION CONCERNING THE PERIODIC SYSTEM OF THE ATOMIC SPECIES

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Introduction

The periodic system of the elements, developed in the years between 1860 and 1870 by de Chancourtois, Newlands, Mendeléef, and Meyer, has now been found to be related to the arrangement and number of the planetary or non-nuclear electrons in the atom. The periods in this system are, respectively, 2, 8, 8, 18, 18, and 32 elements in length. The periodic system of the atomic species, developed between 1915 and the present time by the writer, is an expression of the structure of, and the numerical relations existing in, the nucleus of the atom. The prevailing periodicity in this system is in general expressed by the number 2, although there is superimposed upon this a secondary periodicity of 4. The former number, 2, gives the positive charge on the nucleus of the helium atom (α-particle), while the latter number, 4, expresses the mass of this atom. The theory indicates that the importance of the number, 2, is further magnified by its being the number of negative electrons in the α-particle. The principal purpose of the present paper is to give expression to *a new relation which distinguishes the atomic species of even and of odd atomic weight.* This relation was discovered empirically, while all of the relations found earlier were first discovered by the application of the theory, and were later found to correspond to the facts.

The Periodicities of 2 and 4

Before the discussion of the new relation is entered upon, it is advisable to present the older relations in a simpler form than has been given heretofore. The periodicity of 2 was first noted by Harkins and Wilson,[1] who showed that among the light elements those of odd atomic number have a nuclear composition of one type, while those of even atomic number exhibit quite a different type, provided only the most abundant isotope of each element is alone considered. A little later the writer showed[2] that when abundance of the light elements is plotted against the atomic number, every peak in the abundance curve represents an even-, and every trough, an odd-numbered element. It was shown, also, that there is a very apparent periodicity of 2 in the periods of the most abundant isotopes for the radioactive elements, and the same periodicity in the abundance of these elements, as well as in the number of isotopes per

[1] Harkins and Wilson, This Journal, **37**, 1385, 1391 (1915).

[2] Harkins, *Proc. Nat. Acad. Sci.*, **2**, 216–24 (1916); This Journal, **39**, 856 (1917).

element. These periodicities will not be discussed further in the present paper, since abundant data bearing upon them were given in these earlier papers of the series, but it is essential to refer to them here in order to bring out the full meaning of the periodicities now to be considered.

The periodicity of 2 is here recast in simple form *by expressing it graphically as a double network*. Whether the network takes the form of a set of squares or of figures with curved boundaries depends upon the choice of the variables used for the rectangular coördinates. The 5 variables of experimental significance which are most important in the study of the nucleus of the atom are listed in Table I.

TABLE I

FUNDAMENTAL EXPERIMENTALLY DETERMINED VARIABLES RELATED TO THE NUCLEUS OF THE ATOM

Variable	Experimental significance	Meaning attached by hypothesis
P	Atomic weight	number of protons in nucleus
M	Atomic number	positive charge on nucleus and number of planetary electrons in atom
N	$P-M$	number of negative electrons in nucleus
n	$P-2M$	excess of neutrons in nucleus over the formula $(p_2e)_M$
N/P	$(P-M)/P$	relative negativeness of the nucleus

In this table p represents a proton, and e an electron.

Of the 5 variables listed above, any 2 may be considered as the independent variables, and the other 3 as dependent. When each possible pair of independent variables is plotted on rectangular axes it is easily seen that ten 2-dimensional plots are developed. All of these have been published.[3] The simplest form of plot (Fig. 1), which gives a double network of squares is obtained when the atomic number (M) is chosen as one axis, and the isotopic number (n) as the other.[4] In fact these are the two variables which give rise to the most convenient systems of classification.

In order to simplify Fig. 1, only the first 57 elements, and only the two principal variables, are represented. It will be seen that in this figure heavy lines are used for even numbers, either for the atomic or for the isotopic numbers, while the light lines are used for odd numbers.

In the classification of the atomic species according to the type of line intercepts upon which they lie it becomes apparent that by far the greatest number occur where heavy lines meet. This is shown in Table II.

Thus out of a total of 80 known atomic species, 55% have both atomic and isotopic numbers which are even; in 26.25% both of these numbers are odd; in 15% the atomic number is even, and the isotopic number odd;

[3] Harkins and Madorsky, *Phys. Rev.*, **19**, 135 (1922).

[4] While many of the workers in this field use the variables M and P exclusively, this is only because they do not yet realize that the isotopic number takes the same place in designating the isotope, that the atomic number occupies in fixing the element.

Table II

Classification of the Known Atomic Species in Figure 1 according to the Type of Line Intercepts on which They Lie

	Type of Intercept	Number	N	P
1.	Heavy-heavy	44	Even	Even
2.	Light-light	21	Even	Odd
3.	Vertical heavy-horizontal light	12	Odd	Odd
4.	Horizontal heavy-vertical light	3	Odd	Even

while in only 3.75% is the atomic number odd and the isotopic number even. Thus the rarest event is for the atomic number to be odd while the isotopic number (and atomic weight) is even. Here it may be remarked that since the isotopic number n is equal to $P-2M$, the atomic weight is always odd if the isotopic number is odd, while the atomic weight is always even if the isotopic number is even.

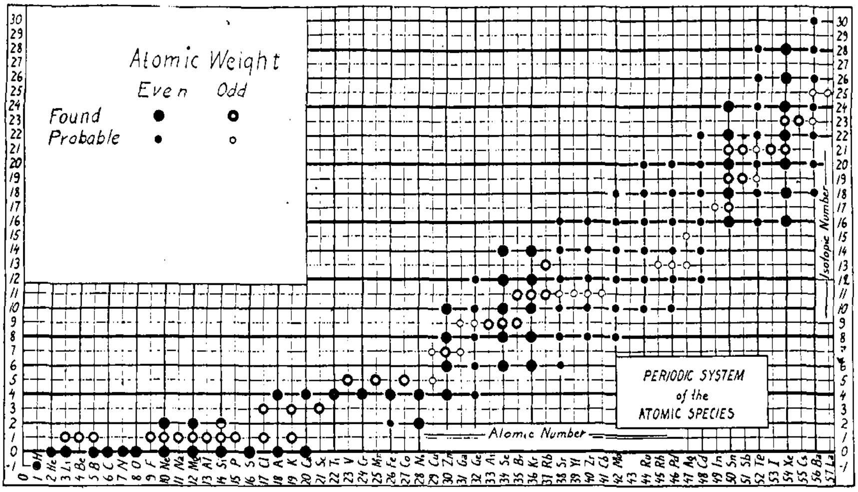

Fig. 1.—Periodic system of the atomic species (isotopes) represented as a double network of squares. This figure shows that the species of even atomic weight give a characteristic pattern of quite a different type from that exhibited by the atomic species of odd atomic weight. The positive-ray work has indicated the existence of the species $10Ne^{21}_{1}$ and $14Si^{30}_{2}$ as doubtful. The mean atomic weight of sulfur indicates that it contains isotopes of higher isotopic number than zero, but the positive-ray work has failed to reveal them. The atomic species 21_3, 22_4, 23_5, 24_4, and 25_5 have not been detected by the positive-ray method, but their mean atomic weight lies closely on the position given and, furthermore, the mean atomic weight corresponds to that predicted for the most abundant isotope by the Harkins-Wilson equation. In no case has an isotope which meets this condition failed of detection when positive-ray measurements upon the element have been made.

Added Note. (Received, May 21, 1923.)—The figure gives definite predictions of the atomic weights (and atomic masses) of the isotopes of elements of odd atomic number in cases where the mean or chemical atomic weight is known with sufficient accuracy. Thus the isotopic numbers for antimony were predicted by the writer as 19 and 21 (atomic weights as 121 and 123) about a year before they were found by Aston, while it was also predicted that cesium would be found to consist of a single isotope of isotopic number 23 (atomic weight 133). The figure indicates the atomic weights of the isotopes of silver as 107 and 109, and *this may be considered a definite prediction*, since the mean atomic weight of silver, 107.88, is known with considerable accuracy. On the other hand it is probable that the mean atomic weight of indium may be more in error, so the isotope listed as of atomic weight 115, may not be the only isotope in this element. Richards' latest atomic weight for gallium (69.716) (This Journal, May, 1923) should be sufficiently accurate so that its isotopes may be predicted definitely as having isotopic numbers 7 and 9, and atomic weights 69 and 71; while those of copper may on the basis of the atomic weight of the element be predicted as having isotopic numbers 5 and 7 (atomic weights 63 and 65). Thus both of the elements with atomic numbers 29 and 31 have atomic species of isotopic number 7, which indicates that the intermediate element zinc, of atomic number 30, should have an isotope of the same isotopic number, and with an atomic weight equal to 67. Thus on the basis of predictions of the isotopes of copper and gallium, Fig. 1, as first drawn, made a secondary prediction of the isotope of zinc of atomic weight 67. When the writer mentioned this prediction to Dr. Dempster he was told that the experimental ionization curves of the latter indicate the existence of such an isotope, but that it is present in such a small quantity that it was not included in the first announcement of the isotopes of this element. Thus a prediction based upon two more primary predictions was proved correct, which demonstrates the remarkable characteristics of the figure.

The base line of Fig. 1, and every fourth horizontal line above it, are made specially heavy to indicate a periodicity of 4 which is superimposed upon the periodicity of two in the vertical direction. Practically all of the high peaks of abundance lie upon these lines. Thus, the most abundant isotope is known for 19 elements of even atomic number listed in Fig. 1, and in 16 of the 19 cases the most abundant isotope lies on one of these specially heavy lines. In only three of the cases is the atomic weight not exactly divisible by 4. In zinc the lowest known isotope of isotopic number 4, is the most abundant, but for higher atomic numbers the most abundant isotope will in general be closer to the middle of the range of stability. However for the elements 34 Se and 36 Kr the most abundant isotope cannot lie exactly in the middle and also have its isotopic number divisible by 4. In both of these cases the isotopic number 12 is the one taken by the most abundant isotope. (Added May 12, 1923. W. D. H.)

A glance at the atomic species of the elements of higher atomic number than 28 shows plainly that the *species of even isotopic number (and even atomic weight) exhibit a pattern which consists of sets of squares made up entirely of heavy lines. That is, the isotopic numbers, the atomic weights, and the atomic numbers are even.* This pattern of the square is also apparent in the atomic species of low atomic number, though on account of the small number of isotopes in this region the pattern is less well filled out. In the cases of argon and calcium the missing of two corners changes what would be a double square on the simplest basis, into a rectangular figure twice as long in the n as it is in the M direction. It will be seen that the general major pattern is thus a step of 2 between adjacent species, along each isotopic line (line of constant atomic number) and even more perfectly, a step of 2 along each isoneutronal line (line of constant isotopic number).

In Fig. 1 each line which represents an isotopic number divisible by 4 is represented by a heavier line than when it is divisible by 2 alone. It will be seen that among the light elements the number of atomic species is particularly high for isotopic numbers 0 and 4. For nearly all of these atomic species the atomic weight is also divisible by 4. In the meteorites more than 92% of all of the atoms have these two isotopic numbers (0 and 4), so the periodicity of 4 is extremely marked among the light elements, both with respect to the isotopic number and the atomic weight. Reference to a figure published earlier[5] will show that this periodicity is prominent in the earth's surface also, though somewhat less striking.

Atomic Species of Odd Atomic Weight and Isotopic Number

It has been seen that if the lines of constant *even* isotopic number are considered, the change of the atomic number for each step between adjacent atomic species is almost always 2, and the atomic number thus remains even. The number of horizontal steps or layers lying one above the other is from 4 to 7, for atomic numbers higher than 28. *On changing to a consideration of the lines of odd isotopic number and atomic weight, a very different pattern is revealed.* Here it seems more common for the change of atomic number along a line of constant isotopic number to be 1, although a change by 2 remains prominent, and instead of from 4 to 7 horizontal steps lying one above another in the region of the heavier elements, there is often only a single step. Also, quite commonly, two steps lie one over the other, but this occurs most generally where there is a transition from a lower to a higher level in going from left to right. In only one case now known do 3 such steps lie above one another, and this is in tin, which is an element of *even atomic number.* Thus far, more than 2 isotopes have in no case been discovered for any non-radioactive element of odd atomic number.

While the periodicity of the pattern under discussion is 2 in the isotopic number, it has been mentioned that it is often 1 in atomic number; however, this means a periodicity of 2 in atomic weight. Thus, whenever on a line of constant isotopic number (isoneutronal line) the atomic number changes by 2, which is the more general change for the whole system, the atomic weight changes by 4 and the nucleus adds one α-particle in going from left to right. However, when the change in the atomic number is only 1, as is common when the isotopic number and the atomic weight are odd, the addition is a half α-particle, or p_2e. Now, it is of great interest that the formula of any atomic species of zero isotopic number is $(p_2e)_M$, since zero isotopic number is the fundamental base line of the system, and no nucleus which is complex is represented by a point below this line. Thus the hypothetical group p_2e seems to play a part which is secondary only to that

[5] Harkins, This Journal, **43**, 1045 (1921).

played by its double, $(p_2e)_2$, which is the α-particle. The writer has suggested the hypothesis that the first step in the formation of an α-particle may be the union of 2 electrons with 1 proton to form the group p_2e, which is very difficult to break up, but readily unites with a like group to form an α-particle. Sometimes it may add to a complex nucleus. The above relation may mean that it adds on more readily when the atomic weight is odd. However, there are so many other ways in which these nuclei might be formed that little weight should be given to this latter hypothesis.

The system followed by the atomic species of odd atomic weight needs expression in a different way from that given above in order that it may be more fully understood. It was supposed by Harkins and Wilson[1] that in general isotopes of elements of even atomic number should have even atomic weights, and elements of odd atomic number should have odd atomic weights. Their supposition has, indeed, been justified. It may be stated, then, that normally elements of odd atomic weight and isotopic number have odd atomic numbers. However, in some exceptional cases the atomic number is even. The question arises, "When does this occur?" This question may be answered empirically by consulting Fig. 1. This figure shows that in all known instances up to and including atomic number 36, *each atomic species of odd atomic weight and even atomic number lies on the* same *isoneutronal line* (line of constant isotopic number) *as, and directly between two adhacent atomic species of next lower and higher odd atomic number.* Thus Be_1^9 lies adjacent to and between Li_1^7 and B_1^{11}. Here the superscript gives the atomic weight, and the subscript the isotopic number. Se_9^{77} lies in the same way between As_9^{75} and Br_9^{79}; Kr_{11}^{83} lies between Br_{11}^{81} and Rb_{11}^{85}; Mg_1^{25} between Na_1^{23} and Al_1^{27}; and Si_1^{29} between Al_1^{27} and P_1^{31}.

As the number of particles in the nucleus increases, which occurs as the atomic and isotopic numbers rise, it is natural to suppose that the occurrence of abnormal types of atomic species would become more frequent, and the relations of periodicity less stringently followed.[6] It is, therefore, not surprising that the condition for the existence of species of odd atomic weight, but even isotopic number, should be less exacting when the atomic number rises as high as 50 to 54. Here, in the elements tin and xenon, the condition seems to be that there shall be one adjacent atomic species of the same isotopic number and of odd atomic number. Thus Xe_{21}^{129} lies just to the right of I_{21}^{127}, but there is no isotope of cesium, of next higher atomic number than xenon, to the right. Also to the right of Xe_{23}^{131} is Cs_{23}^{133}, but to the left there is no isotope of iodine. While the element to the left of tin (indium) has not been tested for isotopes, the mean atomic

[6] The writer has shown that when the number of particles becomes abnormally large, as in the radioactive species, the regularity again increases, due to the fact that the less stable isotopes here become so unstable as to cease to exist in detectable quantities.

weight of indium (which may not be accurate), and the known isotopes of antimony, seem to indicate similar relations for the type of isotopes under discussion, to those found in the case of xenon.[7]

Summary

1. It is found that the periodic system of the atomic species, developed earlier by the writer, can be most simply represented as a double network of lines, atomic species existing only at the intersections of the lines. The simplest double network is given if the atomic number is plotted on one axis (X-axis), while the isotopic number is plotted on the other. In this case a double network of squares is obtained, with alternate heavy and light lines in both directions. It is found that most of the atomic species, and also the most abundant atomic species, occur where both variables are even numbers, that is, where heavy lines intersect each other. The next most favorable type of intersection is that between light lines, where both variables are odd.

2. A moderate number of species of even atomic number but odd isotopic number (and atomic weight) occur, but in general they are not very abundant. In Fig. 1 these lie on heavy vertical, but light horizontal, lines. The occurrence of these species is related in a very direct way to that of odd atomic and isotopic number (and atomic weight), since in general when the atomic number is not too high, each species of odd atomic weight but even atomic number lies on the same line of constant isotopic number as, and directly between 2 atomic species of odd atomic and isotopic numbers (and odd atomic weight).

In the region of atomic number 50 this condition is less exacting, since atomic species of even atomic number but odd isotopic number and atomic weight occur when an atomic species of the same isotopic number is present in either the element of next higher or that of next lower atomic number.

3. In general, species of even atomic weight exist at the intersection of heavy lines, where both the atomic and isotopic numbers are even. For atomic numbers higher than 28, that is, in the region of abundant isotopes, this gives a network of squares, continuous in general within the region of stability, and with from 4 to 7 levels in the vertical or n direction. The general form of the region of stability is that of a hyperbolic band, tangent to the M-axis at the origin.

4. The species of odd atomic weight form a pattern of their own, which is on the whole like a single set of steps, or of stairs, ascending toward the right. In certain limited regions, one step lies directly over

[7] Periodicities of 2 are apparent also in (1) the relative negativeness (N/P) of the nucleus [expressed in a different form in This Journal, **42**, 1984 (1920)] and in (2) the number of negative electrons in the nucleus. *In most atomic species the number of negative nuclear electrons is even. In addition to this it may be stated that all of the most abundant atomic species are included in those in which this number is even.*

another, but the number of overlying steps is very many less than for those which represent the species of even atomic weight.

5. Attention is called to a periodicity of 2 in the number of nuclear negative electrons, and a somewhat less prominent periodicity of 2 in the number of protons. In both of these, *even numbers give predominance over odd numbers in both number of species and in their abundance.*

6. Attention is called also to a periodicity of 2 in the relative negativeness (N/P) of the nucleus.

7. It is found that for constant *even* isotopic number the general difference between adjacent atomic species is 1 α-particle, or p_4e_2. For *odd* isotopic number (and atomic weight) the most common difference is $^1/_2$ α-particle, or p_2e, although the difference of a whole α-particle often occurs, also. Hypotheses concerning these relations are discussed.

8. Fig. 1 predicts the existence of a considerable number of hitherto undiscovered atomic species (isotopes) (consult note to Fig. 1).

9. Of the 19 elements of even atomic number for which in each case the most abundant isotope is known, the atomic weight and the isotopic number are both divisible by 4 in all but three instances. This periodicity is made apparent in the figure by using specially heavy horizontal lines for isotopic numbers divisible by 4.

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UNSATURATION AND MOLECULAR COMPOUND FORMATION. III

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The present paper deals with the tendency of hydrocarbons to form molecular compounds, and a brief outline of previous work and contemporary views may serve as an introduction. The formation of a molecular compound results from the attractive forces between the molecules. These attractive forces in turn must result from particular atoms or groupings of atoms in the respective molecules. Thus the hydrates owe their origin to the residual valence of the oxygen atom which, not being completely compensated by 2 hydrogen atoms, gives to the water molecule a resultant attractive force which may come into play in combining with other molecules. Oxonium compounds also may owe their existence to the residual valence of the oxygen atom. Carbon, on the other hand, is almost completely satisfied by 4 hydrogen atoms, the resultant molecule having a small residual field of force as indicated by melting point, surface tension, and other physical properties: hence, hydrocarbons should show little or no tendency to form molecular compounds. Opposed to this,