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THE CHANGES OF MASS AND WEIGHT INVOLVED IN THE FORMATION OF COMPLEX ATOMS.

[FIRST PAPER ON ATOMIC STRUCTURE.]

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In the study of the important question of the structure and composition of the elements, it might seem that a consideration of the relations existing between the atomic weights should give results of the greatest value. Unfortunately, however, the first suggestions presented to explain the relations which probably exist were given in such a form, and were based upon such extremely inaccurate values for the atomic weights that a very considerable prejudice has been developed against similar hypotheses.

The first important hypothesis in regard to atomic weight relations appeared in two anonymous papers in the Annals of Philosophy for 1815 and 1816, just one hundred years ago. These papers were known to have been written by Prout, whose ideas as they were presented received the vigorous support of Thomson, considered in England as the leading chemical authority of his day; and many years later, from 1840 to 1860, they were very strongly advocated by Dumas, who made a

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[1] This first paper and the second and third papers which follow form the basis for a part of a dissertation presented to the University of Chicago by Ernest D. Wilson in part fulfilment of the requirements for the Ph.D. degree.

large number of atomic weight determinations during this period. Very many other chemists, among them Gmelin, Erdmann, and Marchand, were also numbered among Prout's supporters. On the other hand, Stas, who in the beginning tried to aid Dumas in the revival of Prout's hypothesis, afterward designated it as a pure fiction, and Berzelius at all times adhered to the view that the exact atomic weights could not be determined except by experiment.

The prejudice which existed a few years ago against Prout's idea is well shown by a quotation from von Meyer's History of Chemistry, printed in 1906.

> "During the period in which Davy and Gay-Lussac were carrying on their brilliant work, and before the star of Berzelius had attained to its full luster, a literary chemical event occurred which made a profound impression upon nearly all the chemists of that day, *viz.*, the advancement of Prout's hypothesis. This was one of the factors which materially depreciated the atomic doctrine in the eyes of many eminent investigators. On account of its influence upon the further development of the atomic theory this hypothesis must be discussed here, although it but seldom happens that an idea from which important theoretical conceptions sprang, originated in so faulty a manner as it did."

Prout's work was not, as the above quotation infers, entirely "literary," for he made a large number of experimental determinations for use in his calculations of the specific gravity of the various elements, which he assumed to exist in the gaseous form. His experiments were, according to his own statements, somewhat crude, but he also made use of the more accurate data obtained by Gay-Lussac, and his work was based upon the volume relations of gases as discovered by the French investigator.

Exactly the form in which the numerical part of Prout's hypothesis should be expressed in terms of modern atomic weights, it is difficult to say, but the principal point is that his atomic weights, which, however, are not comparable with those now used, were expressed in whole numbers, as given below in two columns taken from his table:

TABLE I.—PROUT'S TABLE OF THE MORE ACCURATELY DETERMINED ATOMIC WEIGHTS.

Element.	Sp. gr.	Atomic weight, 2 vols. of hydrogen being 1.
H	1	1
C	6	6
N	14	14
P	14	14
O	16	8
S	16	16
Ca	20	20
Na	24	24
Fe	28	28
Zn	32	32
Cl	36	36
K	40	40
Ba	70	70
I	124	124

The atomic weights thus given by Prout are within a few units of the modern values in the case of the univalent atoms and for nitrogen; but the values given for the atoms of higher valence, with the exception of nitrogen, are approximately half the present values. This would mean that according to Prout's system, since the atomic weights he gives are whole numbers, the atomic weights of the present system should be divisible by two for the atoms of higher valence, which is equivalent to the use of the hydrogen molecule instead of the atom as a unit. In this connection it may be noticed that his atomic weights are taken on the basis of "2 volumes of hydrogen being 1."

Thus, from a numerical standpoint, Prout's hypothesis does not seem to mean what is usually supposed. Expressed in terms of the composition of what he considered to be complex atoms, it is given below in his own words:

> "If the views we have endeavored to advance be correct, we may also consider the πρώτη ὕλη of the ancients to be realized in hydrogen, an opinion by the way, not altogether new. If we actually consider this to be the case, and further consider the specific gravities of bodies in their gaseous state to represent the number of volumes condensed into one; or, in other words, the number of the absolute weight of a single volume of the first matter which they contain, which is extremely probable, multiples in weight must also indicate multiples in volume, and *vice versa;* and the specific gravities, or absolute weights of all bodies in the gaseous state, must be multiples of the specific gravity or absolute weight of the first matter, because all bodies in a gaseous state which unite with one another, unite with reference to their volume."

While it is true that Prout had at the time when he presented it, no real foundation for his ideas, more accurate work, while it proved his system to be invalid from a purely numerical standpoint, at the same time established the fact that the atomic weights of the lighter elements, on the hydrogen basis, are much closer to whole numbers than would be likely to result from any entirely accidental method of distribution. Thus the deviations of the lighter elements are small, as will be seen by the following table:

Element.	At. wt. H = 1.	Deviation from a whole number.
He	3.97	0.03
Li	6.89	0.11
Be	9.03	0.03
B	10.91	0.09
C	11.91	0.09
N	13.90	0.10
O	15.88	0.12
F	18.85	0.15

The average of these deviations is 0.09 unit, while the theoretical deviation on the basis that the values for the atomic weights are entirely accidental, is 0.25 unit. If the first seventeen elements are used in the calculation, the average deviation is found to be 0.15 unit, while the re-

TABLE II.—DEVIATIONS OF THE ATOMIC WEIGHTS FROM WHOLE NUMBERS.

	At. wt. H = 1.	Diff. from whole number.	Per cent. variation or the packing effect.	Possible per cent. variation.	At. wt. O = 16.	Diff. from whole number.	Per cent. variation from whole no.	Prob. error in at. wts.
H[1].........	1.000	....	....	....	1.0078	+0.0078	0.78	0.0002
He[2]........	3.97	−0.03	−0.77	12.5	4.00	0.00	0.00	0.01
Li.........	6.89	−0.11	−1.62	7.1	6.94	−0.06	−0.86	0.01
Be.........	9.03	(+0.03)	....	5.5	9.1	+0.1	(+1.11)	0.05
B.........	10.91	−0.09	−0.77	4.5	11.0	0.00	0.00	0.05
C[3].........	11.91	−0.09	−0.77	4.2	12.00	0.00	0.00	0.005
N.........	13.90	−0.10	−0.70	3.6	14.01	+0.01	+0.07	0.005
O.........	15.88	−0.12	−0.77	3.1	16.00	0.00	0.00	0.00
F.........	18.85	−0.15	−0.77	2.6	19.00	0.0	0.0	0.05
Ne[3]........	19.85	....	....	....	20.0	....	....	....
Na[4]........	22.82	−0.18	−0.77	2.2	23.00	0.00	0.00	0.01
Mg.........	24.13	+0.13	+0.55	2.15	24.32	+0.32	+1.33	0.03
Al.........	26.89	−0.11	−0.40	1.85	27.1	+0.10	+0.37	0.1
Si.........	28.08	+0.08	+0.31	1.78	28.3	+0.30	+1.07	0.1
P[5].........	30.78	−0.22	−0.71	1.61	21.02	+0.02	+0.06	0.01
S[3].........	31.82	−0.18	−0.56	1.56	32.07	+0.07	+0.22	0.01
Cl.........	35.19	+0.19	+0.54	1.43	35.46	+0.46	+1.31	0.01
Ar.........	39.57	−0.43	−1.07	1.25	39.88	−0.12	−0.30	0.02
K.........	38.80	−0.20	−0.52	1.28	39.10	+0.10	+0.25	0.01
Ca.........	39.76	−0.24	−0.60	1.25	40.07	+0.07	+0.17	0.03
Sc.........	43.76	−0.24	−0.55	1.14	44.1	+0.10	+0.23	0.2
Ti.........	47.73	−0.27	−0.57	1.04	48.1	+0.10	+0.21	0.1
V.........	50.61	−0.39	−0.77	0.98	51.0	0.0	0.0	0.1
Cr.........	51.60	−0.40	−0.77	0.96	52.0	0.0	0.0	0.05
Mn.........	54.50	−0.50	−0.90	0.90	54.93	−0.07	−0.13	0.05
Fe.........	55.41	−0.59	−1.06	0.89	55.84	−0.16	−0.29	0.03
Co.........	58.51	−0.49	−0.83	0.85	58.97	−0.03	−0.05	0.02

Per cent. variation of 21 elements (omitting Be, Mg, Si, Cl), or the packing effect = 0.77%

Average devation of the atomic weights, H = 1, from whole numbers = 0.21

Theoretical deviation of atomic weights from whole numbers on the basis that the deviations are entirely accidental = 0.25

Average deviation of the atomic weights, H = 1, for the eight elements from helium to sodium = 0.11

Average deviation of the atomic weights, O = 16, when Mg, Si, and Cl are omitted = 0.05

Average deviation of the atomic weights, O = 16, for the eight elements from helium to sodium = 0.02

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[1] W. A. Noyes ("A Text-book of Chemistry," p. 72) states that the atomic weight used for hydrogen, 1.0078, is probably not in error by so much as 1 part in 5000.

[2] Heuse (*Verh. deut. physik. Ges.*, **15**, 518 (1913)) obtained the value 4.002 as the result of 7 experiments.

[3] Leduc (*Compt. rend.*, **158**, 864 (1914)) gives the atomic weight of neon as 20.15 when hydrogen is taken as 1.0075. Leduc's value is not used, on account of the discovery of the complexity of neon as described in the text of the paper.

[4] Richards and Hoover (THIS JOURNAL, **37**, 95 (1915)) determined the atomic weights of carbon as 12.005, and of sodium as 22.995, and in Vol. **37**, p. 108, they give the atomic weight of sulfur as 32.06.

[5] The atomic weight for phosphorus is taken as 31.02 from recent determinations made by Baxter (THIS JOURNAL, **33**, 1657 (1912)).

sult obtained for twenty-five elements is 0.21. The more complete table, designated as Table II, gives these deviations, which are seen to be negative in almost every case, the exceptions being magnesium, silicon, and chlorine. The exclusion of beryllium from consideration in this connection is due to the fact that its atomic weight is not known with sufficient accuracy, and neon is not taken into account, since its positive variation may be explained by the discovery by Thomson and by Aston that neon is a mixture of two isotopes of atomic weights twenty and twenty-two.

Not only is the variation from a whole number a negative number, but in addition its numerical value is nearly constant, the average value for the 21 elements being 0.77%, while the six elements from boron to sodium show values of 0.77, 0.77, 0.70, 0.77, 0.77, and 0.77%. The deviation is therefore not a periodic, but a constant one. If, then, a modification of Prout's hypothesis that the elements are built up of hydrogen atoms as units is to be taken as a working basis, it becomes important to find a cause for the decrease in weight which would result from the formation of a complex atom from a number of hydrogen atoms. The regularity in the effect suggests that, in general, this decrease in weight is probably due to some common cause, though the exceptional cases of magnesium, silicon, and chlorine, show that there is certainly some other complicating factor. The discovery of the reason for the deviation of the same kind in the case of neon, where it is due to its admixture with an isotope of higher atomic weight, suggests that it may not be impossible to find explanations for these three other exceptions. In order to have a term for the percentage decrease in weight, it may be well to call this the packing effect, or the percentage variation from the commonly assumed law of summation, that the mass of the atom is equal to the sum of the masses of its parts.

It has formerly seemed difficult to explain why the atomic weights referred to that of oxygen as 16 are so much closer to whole numbers than those referred to that of hydrogen as one, but, the explanation is a very simple one when the facts of the case are considered. The closeness of the atomic weights on the oxygen basis to whole numbers, is indeed extremely remarkable. Thus for the eight elements from helium to sodium the average deviation is only 0.02 unit, which is less than the average probable error in the atomic weight determinations. When twenty-one elements are taken from the table, omitting the exceptional cases of magnesium, silicon, and chlorine, the deviation averages only 0.05 unit, while if these are included, this is increased only to 0.09 unit. These results have been calculated without taking the sign into account. If the sign is considered the average deviation is reduced to 0.01 unit for the twenty-one elements. The probability that such values could be obtained by accident, is so slight as to be unworthy of consideration. If an oxygen atom is a structure built up from 16 hydrogen atoms, then the weight according to the law of summation should be 16 times 1.0078 or 16.125. The difference between 16.125 and 16.00 is the value of the packing effect, and if this effect were the same for all of the elements, except hydrogen, then the choice of a whole number at the atomic weight of any one of them, would, of necessity, cause all of the other atomic weights to be whole numbers. Though this is not quite true, it is seen that the packing effect for oxygen is 0.77%, which is the average of the packing effects for the other 21 elements considered. Therefore, those elements which have packing effects equal to that of oxygen will have whole numbers for their atomic weights, and since the other elements show nearly the same percentage effect, their atomic weights must also lie close to whole numbers.

According to this view, Prout's hypothesis from the purely numerical standpoint, is entirely invalid, but there still remains the problem of finding an explanation for three facts: First, that the atomic weights of the lighter elements on the hydrogen basis approximate whole numbers; second, that the deviations from whole numbers are negative; and third, that the deviations are practically constant in magnitude. Before considering any explanation of these facts it is of interest to consider the following extremely interesting comments upon this subject, as written by Marignac in 1860:

"We are then able to say of Prout's hypothesis that which we can say of the laws of Mariotte and Gay-Lussac relative to the variations of the volumes of gases. These laws long considered as absolute, have been found to be inexact when subjected to experiments of so precise a nature as those of M. Regnault, M. Magnus, etc. Nevertheless they will be always considered as expressing natural laws, either from the practical point of view. for they allow the change of volume of gases to be calculated in the majority of cases, with a sufficiently close approximation, or even from the theoretical point of view, for they most probably give the normal law of changes of volume, when allowance has been made for some perturbing influences which may be discovered later. and for which it may also be possible to calculate the effects. We may believe that the same is true with respect to Prout's law; if it is not strictly confirmed by experiment, it appears nevertheless to express the relation between simple bodies with sufficient accuracy for the practical calculations of the chemist, and perhaps also the normal relationship which ought to exist among these weights, when allowance is made for some perturbing causes, the research for which should exercise the capacity and imagination of chemists. Should we not, for example, quite in keeping with the fundamental principle of this law, that is to say, in admitting the hypothesis of the unity of matter. be able to make the following supposition. to which I attach no further importance than that of showing that we may be able to explain the discordance which exists between the experimental results and the direct consequences of this principle? May we not be able to suppose that the unknown cause (probably differing from the physical and chemical agents known to us), which has determined certain groupings of primordial matter so as to give birth to our simple chemical atoms. and to impress upon each of these groups a special character and peculiar properties. has been able at the same time to exercise an influence upon the manner in which these groups of atoms obey the law of universal attraction, so that the weight of each of them is not exactly the sum of the weights of the primordial atoms which constitute it?"

It has usually been assumed, and without any really logical basis for the assumption, that if a complex atom is made up by the union of simple atoms, the mass of the complex atom must be exactly equal to the masses of the simple atoms entering into its structure. Rutherford, from data on the scattering of α-rays in passing through gold leaf, has calculated an *upper* limit for the radius of the nucleus of a gold atom as 3.4×10^{-12} cm. The mass of this relatively heavy atom is, according to this calculation, practically all concentrated in this extremely small space, which is so small that it could no longer be expected that the mass of such a nucleus, if complex, would be equal to the sum of the masses of its component parts. In fact, since the electromagnetic fields of the electrons would be so extremely closely intermingled in the nucleus, it would seem more reasonable to suppose that the mass of the whole would not be equal to the sum of the masses of its parts. The deviation from the law of summation cannot be calculated on a theoretical basis, but it can easily be determined from the atomic weights, if the assumption is made that the heavier atoms are condensation products of the lightest of the ordinary elements, that is of hydrogen. This deviation expressed in terms of the percentage change, is what has already been determined, and designated as the packing effect.

Since this packing effect represents a decrease in weight, the first problem which represents itself for determination is the *sign* of the effect which would result from the formation of the positively charged nucleus of an atom by the combining of positive and negative electrons into some form of structure. Richardson[1] suggests that the positive nucleus of an atom might be built up of positive electrons alone and still be stable if the law of force between them were

$$+ a/r^2 - b/r^{p_1} + c/r^{p_2}, \text{ where } p_2 > p_1 > 2.$$

Here the first term gives the usual law of force, the second causes the electrons when close together to attract each other, and the third expresses the repulsion which keeps them from joining together. It would, however, seem more simple to assume, what seems much more probable, that the nucleus is held together by the attraction of positive and negative electrons, both of which are assumed to be present in any complex nucleus.

Since, even when the mass is assumed to be entirely electromagnetic, there still remain two possibilities even for the simple case of hydrogen, first, that the hydrogen nucleus is the positive electron, and second, that it may be complex, it has seemed best to choose for the purpose of cal-

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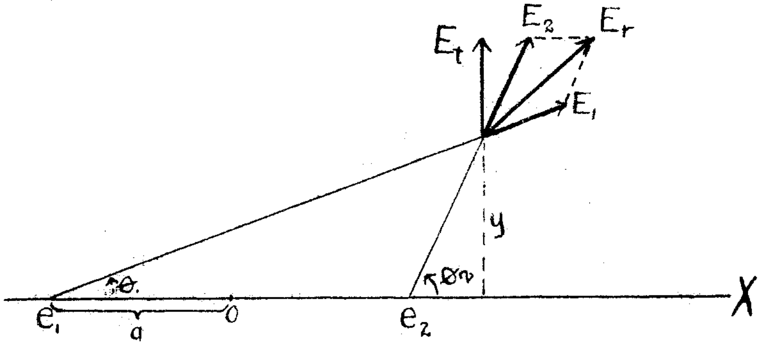
[1] "The Electron Theory of Matter," p. 582.

culation the simplest system, which consists of one positive and one negative electron. The problem thus presented for solution is the determination of the sign and the magnitude of the change of mass which results when a positive and a negative electron are brought extremely close together.



Lorentz[1] speaks of this problem, but does not solve it either with respect to the sign or the magnitude of the effect. He does state, however, that if the electrons were to be brought into immediate contact, the total energy could not be found by addition, which may be considered as equivalent to the statement that the mass of a system made up in this way would not be the same as the sum of the masses of its parts. The fundamental equations used here as the basis of the calculation which follows, have been taken from the work of Lorentz.

The value of e, the charge on the electron, may be defined as

$$e = \iiint \rho d\tau,$$

where ρ is the volume density of the electricity, and $d\tau$ is an element of volume. For the purposes of the first part of the calculation, the electron may be considered as a point charge, but the values of the electromagnetic mass used later are given for the Lorentz form of electron, which takes the form of an oblate spheroid when in motion.

The space surrounding an electron must be considered as different from a space not adjacent to an electrical charge. If a charged particle is brought into this space it is acted upon by a force which varies from point to point, and has at every point in space a definite value and direction. This force is designated by **E**, and is a vector point function. If the electron is in motion it acts as an electric current equal to eu, where u represents its velocity. The magnetic force due to this motion is easily seen to be a function of the current equivalent of the moving electron, and is also a vector, designated by **H**. Then

$$\mathbf{H} = f(\mathbf{E}, u, \phi)$$

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[1] H. A. Lorentz. "The Theory of Electrons." 1909, pp. 47 and 48.

where ϕ is the angle between **E** and the direction of motion. The direction of **H** is perpendicular to the direction of u and is at the same time circular.

It is evident that the total energy of the system is a function of both the electric and the magnetic intensities. For the purposes of this calculation the mass of a system is considered as electromagnetic, and hence as a function of the energy of the system. Therefore it is necessary to use some function of both **E** and **H**. This function is designated by **G** and is called the electromagnetic momentum. The derivation of the equations for **G** has been given by Lorentz, so here it will be sufficient to define it as

$$\mathbf{G} = [\mathbf{E}\,\mathbf{H}]/c$$

where [**E H**] means the vector product of **E** and **H**, and c is the velocity of light. From the expressions obtained for **G** it is easy to obtain those which represent the mass.

In the treatment which follows, only the longitudinal electromagnetic mass is considered, and terms containing u to a higher power than the first are disregarded, as they appear to be unimportant. The following general treatment, in which Heaviside units are used, gives an outline of the method:

For the field due to a system of charges

$$\frac{[\mathbf{EH}]}{c} = \frac{[(\Sigma_i\mathbf{E}_i)(\Sigma_j\mathbf{H}_j)]}{c} = \frac{\Sigma_i[\mathbf{E}_i\mathbf{H}_i]}{c} + \frac{\Sigma_{(ij)}[\mathbf{E}_i\mathbf{H}_j]}{c}$$

where the summation $\Sigma_{(ij)}$ is the vector product of each i with each j. The first summation gives the electromagnetic momentum which would be due to the particles if their fields did not overlap, and the second term, which is the important one here, gives the effect of the overlapping of the fields. This may be called the "mutual electromagnetic momentum" and designated by $\overline{\mathbf{G}}$.

For point charges

$$\mathbf{E}_1 = \frac{(1 - u^2)e_1}{4\pi r^2(1 - u^2 \sin^2 \theta_1)^{3/2}}$$

at the point $P_{x,\,y,\,z}$. Let

$$(1 - u^2 \sin^2 \theta_1) = \beta_1^2$$

and

$$(1 - u^2) = k^2.$$

The transverse component of **E** due to the two particles 1 and 2 is

$$\mathbf{E}_t = \frac{k^2 e}{4\pi}\left\{\frac{\sin \theta_2}{\gamma_1{}^2\beta_1{}^3} \pm \frac{\sin \theta_2}{\gamma_2{}^2\beta_2{}^3}\right\}$$

where the sign is *positive* if the charges have the same sign, and *negative* if they are of opposite sign. As only the longitudinal component of the vector **G** is desired, only the transverse component of **E** is needed.

$$\mathbf{H} = u/c\ \mathbf{E} \sin \phi$$

where ϕ = the angle between $\mathbf{E}$ and the direction of u. If $\mathbf{E}_t'$ is used $\phi = 90°$. Therefore

$$\mathbf{H} = u/c\ (\mathbf{E}_1 \sin \theta_1 \pm \mathbf{E}_2 \sin \theta_2)$$

$$\mathbf{G}_{\mathrm{L}} = \frac{[\mathbf{E}_t\mathbf{H}]}{c} = \frac{u}{c_2}\ (\mathbf{E}_1 \sin \theta_1 \pm \mathbf{E}_2 \sin \theta_2)(\mathbf{E}_1 \sin \theta_1 \pm \mathbf{E}_2 \sin \theta_2).$$

And

$$\overline{\mathbf{G}} = \pm \frac{2u}{c^2} \int \mathbf{E}_1\mathbf{E}_2 \sin \theta_1 \sin \theta_2\, d\tau$$

$$= \pm \frac{2u}{c^2}\ \frac{k^4e^2}{(4\pi)^2} \int \frac{\sin \theta_1 \sin \theta_2}{\gamma_1{}^2\gamma_2{}^2\ \beta_1{}^3\beta_2{}^3}\, d\tau.$$

Now

$$\gamma^2\beta^2 = \gamma^2 - u^2(\gamma^2 \sin^2 \theta) \quad \text{and} \quad (\gamma^2 \sin^2 \theta) = y^2.$$

Neglect all of the terms in u^2.

$$d\tau = 2\pi y dy dx.$$

Then

$$\overline{\mathbf{G}} = \frac{uk^4e^2}{8c^2\pi^2} \cdot 2(2\pi) \int_0^\infty \int_0^\infty \frac{y^3 dy dx}{\sqrt{\{[(x-a)^2+y^2][(x+a)^2+y^2]\}^3}}$$

which is obtained by making use of the symmetry of the equation. Or

$$\overline{\mathbf{G}} = \left(\frac{uk^4e^2}{8c^2\pi^2} \cdot 4\pi\right)\frac{1}{a} \int_0^\infty \int_0^\infty \frac{y^3 dx dy}{\sqrt{\{[(x-1)^2+y^2][(x+1)^2+y^2]\}^3}}$$

$$= \frac{uk^4e^2}{2\pi c^2 a}\, \mathrm{J}$$

where

$$\mathrm{J} = \int_0^\infty \int_0^\infty \frac{y^3 dx dy}{\sqrt{\{[(x-1)^2+y^2][(x+1)^2+y^2]\}^3}}$$

$$\mathrm{J} = \frac{1}{2}\int_0^\infty dx \int_0^\infty \frac{udu}{[(\alpha+u)(\beta+u)]^{3/2}}$$

where $u = y^2$.

$$\alpha = (x-1)^2; \quad \beta = (x+1)^2; \quad \alpha - \beta = (-4x).$$

$$\mathrm{J} = \frac{1}{2}\int_0^\infty dx \left[\frac{2[(\alpha+\beta)u + 2\alpha\beta]}{(\alpha-\beta)^2[(\alpha+u)(\beta+u)]^{1/2}}\right]_0^\infty$$

$$= \int_0^\infty \left[\frac{(\alpha+\beta)}{(\alpha-\beta)^2} - \frac{2\alpha\beta}{(\alpha-\beta)^2\sqrt{\alpha\beta}}\right] dx$$

$$= \int_0^\infty \frac{1}{16x^2}\,[\alpha+\beta-2\sqrt{\alpha\beta}]\, dx$$

$$= \int_0^\infty \frac{[\sqrt{\alpha}-\sqrt{\beta}]^2}{16x^2}\, dx$$

$$= \int_0^\infty \frac{[(x-1)-(x+1)]^2}{16x^2}\, dx$$

$$= \int_0^1 \frac{(-2x)^2}{16x^2}\,dx + \int_0^\infty \frac{(-2)^2}{16x^2}\,dx$$

$$= \frac{1}{4} + \frac{1}{4}$$

$$= \frac{1}{2}$$

$$\therefore \overline{G} = \frac{uk^4e^2}{4\pi ac^2}$$

The mass represented by this value of $\overline{G}$ is

$$\Delta m = \pm e^2/4\pi c^2 a.$$

Now the longitudinal mass, m_1 is

$$m_1 = e^2/6\pi c^2 R,$$

where R is the radius of the electron. By division

$$\Delta m/m_1 = 3R/2a,$$

where a is equal to one-half the distance apart of the electrons.

In the application of this last equation, R must be taken as the radius of the positive electron, since it is assumed that it is the seat of practically all of the mass of the atom. For a decrease of mass of 1% in this simple case the distance apart of the positive and negative electrons would be, according to the equation, 300 times the radius of the positive electron. In order to produce a decrease of mass equal[1] to the average decrease of weight found for the 21 elements given in Table II, or 0.77%, the distance apart of the two electrons as calculated, would be 400 times the radius of the positive electron. This, however, does not give the result for any actual case which is known, and in general the nucleus of an atom must be more complex than this. In a more complex nucleus it is possible that the positive and negative electrons need not come so close together in order to give the same decrease of mass. It is evident that the calculation cannot be applied to any special atom until the mass of the positive electron is determined. If, as Rutherford seems to think probable, the positive nucleus of the hydrogen atom is the positive electron, then the most probable composition of the helium nucleus would be four positive electrons to two which are negative, and it would not seem improbable that in such a system the effect upon the mass of the positive electrons might be greater than in the simpler case used for the calculation, which would mean simply that the positive and negative electrons need not be so close together to produce the same effect on the mass. Whether this is true or not could not be determined without a knowledge of the structure of the helium nucleus. If, as Nicholson assumes, the

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[1] From the electromagnetic theory the velocity of high speed electrons also exerts a perceptible influence upon the mass, but the magnitude of this effect has not as yet been determined for the case of the electrons in an atom.

hydrogen nucleus is complex, the decrease of mass in the formation of one helium atom from four of hydrogen, would be due to the closer packing of the positive and negative electrons in the helium nucleus.

Earlier in the paper it has been shown that the fact that the atomic weights on the oxygen basis are much closer to whole numbers than those on the hydrogen basis, is explained by what has been called the packing effect, or the change of mass involved in the formation of heavier atoms from hydrogen. The average of the packing effects for the elements considered, is 0.77%. This is also the value of this effect for oxygen, which happens to have been chosen as the fundamental element in the determination of atomic weights. If the number representing atomic weight of hydrogen, 1.0078, is decreased by this percentage amount, it becomes 1.0000, which is the fundamental unit in atomic weight determinations. The atomic weights of the twenty-five fundamental elements listed in Table II, are found, on the whole, to be very nearly products of this unit by a whole number. While the numerical unit of measurement does not change, the actual unit of mass, the mass of the hydrogen nucleus, varies slightly from atom to atom, and this variation causes the slight deviation of the atomic weights from whole numbers.

The opposite of the system here proposed would be, to suppose that the values of the atomic weights are wholly the result of accident. On this basis the probability that the atomic weights fall as close to whole numbers as they do, may be calculated. In such calculations oxygen is omitted, since its atomic weight is fixed as a whole number, and hydrogen is not used, since its atom contains only one hydrogen nucleus.

The first calculation made was that of the probability that *each* of the atomic weights should be as close as it is to a whole number. The data used are those of Table II. The chance that the atomic weight of nitrogen should entirely, by accident, deviate from a whole number by only 0.01 of a unit was determined by dividing the unit into the 200 divisions corresponding to the assumed accuracy (Landolt-Börnstein-Meyerhoffer, Tabellen) of 0.005. The greatest possible deviation would then be 100 divisions, while the actual deviation of 0.01 unit corresponds to 2 divisions. The probability is then one-fiftieth. The chance that any number of independent events should all happen is the product if the separate probabilities of their each happening. The probability calculated in this way is 2×10^{-22}, or

$$\frac{2}{10{,}000 \text{ billion billion}},$$

which indicates that there is practically no chance that the atomic weights are entirely the result of accident.

Another probability, which seems to be of more value in connection with the present problem, is that the *sum* of the deviations shall not exceed the sum actually found. This is of the form known as De Moivre's problem, and the method was used by Laplace[1] in calculating the probability that the sum of the inclinations of the orbits of the ten planets to the ecliptic is not greater than the value found at that time, 0.914187 of a right angle. The result obtained was 1.1×10^{-7}. The problem is stated in the following way: An urn contains $n + 1$ balls marked, respectively, 0, 1, 2, 3, ... n; a ball is drawn and replaced: required the probability that after i drawings the sum of the numbers drawn will be s. This probability is the coefficient of x^s in the expansion of

$$\frac{1}{(n+1)^i}(1 - x^{n+1})^i(1 - x)^{-i},$$

or the probability P is

$$P = \frac{1}{(n+1)^i}\left\{\frac{\underline{|i+s-1}}{\underline{|i-1}\,\underline{|s}} - \frac{i}{1}\,\frac{\underline{|i-1+s-n-1}}{\underline{|i-1}\,\underline{|s-n-1}} + \frac{i(i-1)}{1.2}\,\frac{\underline{|i-1+s-2n-2}}{\underline{|i-1}\,\underline{|s-2n-2}}\cdots\right\}.$$

In the case of the atomic weights P gives the probability that the sum of the deviations from whole numbers shall equal s, which is not what is desired. The result wanted is the probability that the sum of the errors shall be equal to or less than s, or the summation of the Ps from 0 to s. Now

$$\sum_{s=0}^{s=s}\frac{\underline{|i+s-1}}{\underline{|i-1}\,\underline{|s}} = \frac{\underline{|i+s}}{\underline{|i}\,\underline{|s}}$$

So the desired probability, P′ is:

$$P' = \sum_{s=0}^{s=s}P = \frac{1}{(n+1)^i}\left\{\frac{\underline{|i+s}}{\underline{|i}\,\underline{|s}} - \frac{i}{1}\,\frac{\underline{|i+s-n-1}}{\underline{|i}\,\underline{|s-n-1}} + \frac{i(i-1)}{1.2}\,\frac{\underline{|i+s-2n-2}}{\underline{|e}\,\underline{|s-2n-2}} - \frac{i(i-1)(i-2)}{1.2.3}\,\frac{\underline{|i+s-3n-3}}{\underline{|i}\,\underline{|s-2n-3}}\cdots\right\}.$$

In solving this problem all of the first twenty-seven elements have been used with the exception of hydrogen and oxygen, and these *should* be omitted for the reasons given above. The errors in the determined values have been taken as they are given in Table II. The atomic weights used in the calculation are as follows:

He..........	4.002	Mg.........	24.32	Ca...........	40.07
Li...........	6.94	Al..........	27.1	Sc...........	44.1
Be..........	9.1	Si...........	28.3	Ti...........	48.1
B...........	11.0	P...........	31.02	V............	51.0
C...........	12.005	S...........	32.06	Cr...........	52.0
N...........	14.01	Cl..........	35.46	Mn..........	54.93
F...........	19.00	A...........	39.88	Fe...........	55.84
Ne..........	20.15	K...........	39.10	Co...........	58.97
Na..........	22.995				

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[1] Laplace, "Oeuvres VII, Theorie Analytique des Probabilites," pp. 257–62.

The average probable error as determined from Table I is 0.043 unit, which is equivalent to about 24 divisions for one unit, or 12 divisions for half a unit, which is the maximum possible deviation from a whole number. Since n is 12, $n + 1$ is taken as 13. The sum of the deviations from whole numbers is 2.342, which is equal to 56 of the divisions determined above, or $s = 56$. The number of elements, i, is 26. The probability calculated on this basis is 6.56×10^{-8}, or approximately

$$\frac{1}{15,000,000}.$$

It has been assumed in this paper that the cause of the deviations of neon, magnesium, silicon, and chlorine, which are exceptional in giving positive deviations from the atomic weights on the hydrogen basis, must be different from that which gives the deviations of the other elements. The cause of the deviation of neon has been explained, but for the others it is unknown. In the calculations of the probabilities given above these elements have been included. It may be of interest to note that if these elements had been excluded the probability for the 21 remaining elements would have been found to be about

$$\frac{1}{7 \text{ billion}}.$$

It is an interesting coincidence that the probability above found for the 27 lighter elements is about 1×10^{-7}, while the probability determined by Laplace that the sum of the inclinations of the ten planets then known, to the ecliptic, should not be greater than the sum of the measured values, is almost the same, or 1.123×10^{-7}. In the second paper of this series it will be shown that the atomic weights not only approximate whole numbers, but that these whole numbers are in addition *certain* numbers which are determined by a special system, and which may be given accurately by an equation of the form

$$W = 2(n + n') + {}^1/_2 + [(-1)^{n-1} \times {}^1/_2].$$

The probability that the atomic weights should come so close to these *special* whole numbers is much less than that calculated above, so that the words of Laplace may be applied to the system presented here, as well as to the one he himself gives. That the atoms are built up of units of weight very close to one, and that therefore this modified form of Prout's hypothesis holds, "est indiquee avec une probabilite bien superieure a celle du plus grand nombre des faits historiques sur lesquels on ne se permet aucun doute."

The accepted atomic weights on the oxygen basis as now used are closer to whole numbers than those given by Ostwald in 1890.[1] Ostwald's numbers are all larger than the corresponding whole numbers, so the

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[1] *Allgemeine Chemie*, 1, p. 126 (1890).

deviations were all positive. On the other hand, the present values show both positive and negative deviations. The fact that the small change of 0.77% from the oxygen to the hydrogen basis eliminates practically all of the tendency of the atomic weights to be near whole numbers, when as many as 27 elements are considered as in Table II, shows that the atomic weight of oxygen cannot be taken as very different from 16.00 without obscuring this relationship. Thus it has been shown that the probability that the atomic weights on the oxygen basis would come entirely by accident as close to whole numbers as they do, is 6.56×10^{-8}, or about

$$\frac{1}{15,000,000}.$$

A change of only 0.77% from the oxygen basis causes an enormous increase in the probability that the atomic weights obtained in this way could be as close to whole numbers as they are, entirely by accident. Thus the chance that the sum of the deviations should come out as equal to, or less than, the sum actually found, is 0.105, or

$$\frac{1}{10}.$$

As has been seen, there are 27 atomic weights distributed over 59 units of atomic weight. The greatest common divisor of the whole numbers corresponding to the atomic weights is one. The atomic weights are therefore such that numerically they seem to be built up from a unit of a mass of one, and the probability results seem to show that this unit of mass must be very close to 1.000, expressed to three decimal places. On the other hand, this unit of mass must be somewhat variable to give the atomic weights as they are, even although a part of the variation, in some cases, may be due to the inaccuracy with which the atomic weights are known. This leads either to the supposition (1) that the atoms are built up of some unknown elementary substance, of an atomic weight which is slightly variable, but is on the average extremely close to 1.000, and which does not in any case deviate very far from this value, or to the idea (2) which is presented in this paper, that the *nucleus* of a known element is the unit of structure. The atom of this known element has a mass which is close to that of the required unit, and it has been proved that the decrease of mass involved in the formation of a complex atom from hydrogen units is in accord with the electromagnetic theory. The adoption of the first hypothesis would involve much more complicated relations. It would necessitate the existence of another elementary substance with an atomic weight close to that of hydrogen, it would involve a cause for the increase of weight in the formation of some atoms, and a decrease in other cases, and it would also involve the existence of another unit to give the hydrogen atom.

In the second paper, which follows, still more evidence in favor of the theory that the other atoms are complex atoms built up from hydrogen units will be presented, and it will be shown that there is also an important secondary unit of structure.

The writers wish to thank Professor A. C. Lunn, of the Department of Mathematics, for outlining for them the mathematical analysis of the determination of the packing effect.

Summary.

1. The atomic weights of the first 27 elements, beginning with helium, are not multiples of the atomic weight of hydrogen by a whole number, as they would be if Prout's original hypothesis in its numerical form were true. This may be expressed by the statement that the atomic weights on the hydrogen basis are not whole numbers. However, when these atomic weights are examined critically it is found that they differ from the corresponding whole numbers by a nearly constant percentage difference, and that the deviation is negative in sign, with an average value of —0.77%.

2. This percentage difference has been called the packing effect, and it represents the decrease of weight, and presumably the decrease of mass, which must take place if the other atoms are complexes built up from hydrogen atoms. The regularity in this effect is very striking, the values for a number of the lighter atoms being as follows: He, —0.77; B, —0.77; C, —0.77; N, —0.70; O, —0.77; F, —0.77; and Na, —0.77%, while the average value for the first 27 elements is —0.77%.

3. The regularity of the packing effect gives an explanation of the well-known fact that the atomic weights on the oxygen basis are very close to whole numbers, while this is not true of the atomic weights on the hydrogen basis except in the case of the lightest elements from helium to oxygen. The atomic weight of hydrogen on the oxygen basis is 1.0078. If this were decreased by the value of the packing effect of 0.77%, it would become a whole number, 1.000. Then, if the other elements are built up from hydrogen atoms as units, all of the atoms which are formed with a packing effect of —0.77%, must have whole numbers for their atomic weights; thus the atomic weights of the elements listed in Section 2, above, must be whole numbers in six of the seven cases listed, He, B, C, O, F, and Na. The fixing of any one of these six atomic weights as whole numbers causes the other five to be whole numbers also. Thus the atomic weights referred to carbon as 12.00 would be the same as those referred to oxygen as 16.00. A variation of the atomic weight of an element on the oxygen basis from a whole number indicates that the packing effect for that element does not have the average value.

4. Recent work has shown that the nucleus of an atom must be extremely minute. Thus Rutherford gives the *upper* limit for the radius

of the relatively large and complex gold atom as 3.4×10^{-12} cm., while Crehore, who proposes another theory of the structure of the atom, considers that none of the electrons have orbits of a greater radius than 10^{-12} cm. The high velocity with which the β-particles are shot out in radioactive transformations has been considered as evidence that these electrons must come from much closer to the center of the atom than the assumed radius of the atom. It therefore seems practically certain that the electrons and positively charged particles which make up the nucleus of a complex atom, are packed exceedingly closely together. As a result of this close packing, the electromagnetic fields of the charged particles must overlap to a considerable extent, which would mean that the mass of the atom ought not to be equal to the sum of the masses of the individual particles from which it is built.

5. The closeness to which a positive and a negative electron would have to approach to give a decrease of mass equal to 0.77%, or the average value of the packing effect, is found by calculation to be to a distance of 400 times the radius of the positive electron. This case does not correspond to any element actually known, for the simplest of the atoms considered, helium, may be supposed to have a nucleus built up from four hydrogen nuclei and two negative electrons. However, the magnitude of the effect seems to be of the order which would be expected.

6. The probability for the first 27 elements, that the sum of the deviations of the atomic weights (on the oxygen basis from whole numbers) should by accident be as small as it is, is found to be one chance in fifteen million. On the other hand, a change of only 0.77% from the oxygen basis to that of hydrogen gives one chance in ten that the atomic weights should be as close to whole numbers as they are.

The second paper on atomic structure, which follows this one, gives still more evidence that the complex atoms are built up from hydrogen atoms as units of structure.

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[CONTRIBUTION FROM THE KENT CHEMICAL LABORATORY OF THE UNIVERSITY OF CHICAGO.]

THE STRUCTURE OF COMPLEX ATOMS. THE HYDROGEN-HELIUM SYSTEM.

[SECOND PAPER ON ATOMIC STRUCTURE.]

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In the preceding paper it has been shown that the atomic weight relations of the elements are such as to make it extremely probable that the atoms are complex structures built up from hydrogen atoms. It therefore becomes important to determine in what way the hydrogen atoms unite