ELECTRONIC FREQUENCY AND ATOMIC NUMBER.

By Paul D. Foote.

IN three recent papers[1] Dr. Allen has attempted to show that a relation exists between atomic frequency and atomic number such that the product of Moseley's atomic number N and the characteristic frequency ν for an element in the solid state can be expressed in the form $N\nu = n\nu_0$ where n is an integer or in a few cases an integer plus a simple fraction such as $\frac{1}{2}$ or $\frac{1}{4}$, and ν_0 is a constant fundamental frequency. In the case of electronic frequencies a similar relation is claimed. Thus for ionization potentials, the Einstein equation $eV = h\nu$ may be written $eV = hn\nu_0/N$ where n is the characteristic integer and ν_0 the fundamental frequency. Also since $h\nu_0 = eV_0$ where V_0 is the fundamental potential corresponding to the frequency ν_0 we have that $V = nV_0/N$. Dr. Allen tested this relation for 7 elements and concluded that $V_0 = 13.5$ volts. According to the Bohr theory, the work required to move an electron from the mth orbit to the nth orbit of a hydrogen atom is given by the following equation:

$$\text{(1)} \qquad \text{Work done} = K\left(\frac{1}{m^2} - \frac{1}{n^2}\right),$$

where K is Rydberg's constant. When $m = 1$ and $n = \infty$ we obtain the work required to ionize the atom. Expressed in equivalent volts the value 13.5 volts is obtained, which is identical with the expression for V_0 above. Thus, the ionization potential for any element appears to be equal to the ionization potential for the hydrogen atom multiplied by the ratio of the characteristic integer and the atomic number of the element in question.

Within the past three months, since the papers by Dr. Allen were written, a considerable amount of data has been published on the subject of ionization potentials. Values determined by Franck and Hertz, Davis and Goucher, Bazzoni, Tate, Tate and Foote, Foote and Mohler, Hughes and Dixon, and in a few cases theoretical values concerning which there can be no question whatever are summarized in Table I. When several determinations have been made for the same element, a mean value has been chosen. The fourth column gives the product of the

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[1] H. Stanley Allen, Phil. Mag., 34, p. 478, 1917; idem, 34, p. 488, 1917; Proc. Roy. Soc. Lond., 94, p. 100, 1917.

atomic number and the ionization potential. In the case of six elements the resonance potential is also included as indicated in column 3. It will appear from this table that the product NV can be represented by nV_0 where V_0 is equal to 10.16 volts, and n is an integer (with the exception of three cases where it is an integer plus a simple fraction).

TABLE I.

Atomic Numbers and Ionization Potentials.

Element.	Atomic Number N	Ionization Potential V.	NV.	$n \cdot V_0$.	ΔV_0.	Computed Ionization Potential $V = n\overline{V}_0/N$.	± (Observed − Computed) ΔV.
H.....	1	10.5	10.5	$1 \cdot 10.50$	.36	10.2	.3
He....	2	20.2	40.4	$4 \cdot 10.10$	.06	20.3	.1
N.....	7	7.5	52.5	$5 \cdot 10.50$	.36	7.3	.2
Na....	11	5.11	56.2	$5\frac{1}{2} \cdot 10.22$	.06	5.08	.03
O.....	8	9.1	72.8	$7 \cdot 10.40$	.24	8.9	.2
K.....	19	4.32	82.1	$8 \cdot 10.26$	.10	4.28	.04
Mg....	12	7.61	91.3	$9 \cdot 10.14$	.02	7.62	.01
Ca....	20	6.08	121.6	$12 \cdot 10.13$	.03	6.10	.02
S.....	16	8.3	132.8	$13 \cdot 10.22$	.06	8.3	.0
Cl.....	17	8.2	139.4	$14 \cdot 9.96$	.20	8.4	.2
Ne....	10	16.	160.	$16 \cdot 10.00$	.16	16.3	.3
A.....	18	12.	216.	$21 \cdot 10.29$	.13	11.9	.1
Sr.....	38	5.67	215.5	$21 \cdot 10.26$	.10	5.62	.05
Zn....	30	9.35	280.5	$28 \cdot 10.02$	.14	9.48	.13
Ba....	56	5.12	286.7	$28 \cdot 10.24$	.08	5.08	.04
Br....	35	10.	350.	$35 \cdot 10.00$	.16	10.2	.2
Cd....	48	8.95	430.	$43 \cdot 10.00$	.16	9.10	.15
Hg....	80	10.4	832.	$83 \cdot 10.02$	.14	10.54	.14
		Resonance					
Na....	11	2.10	23.1	$2\frac{1}{4} \cdot 10.27$	.11	2.08	.02
K.....	19	1.60	30.4	$3 \cdot 10.13$	.03	1.61	.01
Mg....	12	2.68	32.2	$3\frac{1}{4} \cdot 9.91$	.25	2.75	.07
Zn....	30	4.02	120.6	$12 \cdot 10.05$	.11	4.06	.04
Cd....	48	3.79	181.9	$18 \cdot 10.11$	.05	3.81	.02
Hg....	80	4.9	392.	$39 \cdot 10.05$	.11	4.95	.05

Mean $V_0 = \overline{V}_0 = 10.16 \pm 0.13$ av. dev.

The seventh column of Table I. gives the ionization potentials computed from the relation $V = nV_0/N$ where $V_0 = 10.16$, and the last column shows the deviations between these computed values and the observed values. The average deviation is ± 0.13 volt, which is about the accuracy of any of the experimental work. Thus, the relation proposed by Dr. Allen appears confirmed with the exception that $V_0 = 10.16$ volts instead of 13.5 volts. There is, moreover, possibly as much theoretical justification for the value 10.16 volts as for the value 13.5

volts. Referring to equation (1) we find that the work required to move the electron from the first to the second ring of the hydrogen atom is:

$$K\left(\frac{1}{1^2}-\frac{1}{2^2}\right)\text{ equivalent to 10.1 volts.}$$

Hence, instead of relating all ionization potentials to the work required to ionize a hydrogen atom, the above table shows that they can be related to the work required to move an electron from the first to the second ring of the hydrogen atom.

In spite of the surprising accuracy of this relation based on the value $V_0 = 10.16$ there is considerable doubt, in the absence of any real theoretical justification, that a relation of the above type can be postulated from a purely empirical basis. Thus, the above table confirms the value of $V_0 = 10.16$, but nearly as good results may be obtained with $V_0 = 8.09$, 8.51, 9.15, 9.45, 9.91, 10.16, 10.29, 10.49 and 10.85. However, as Dr. Allen has pointed out, little weight can be attached to the computation of the integers n when the product NV is large. On the other hand, the experimental data happen to be very unsatisfactory for the elements for which NV is small. Accordingly we feel justified in including the more accurate data for the elements of higher atomic number, as listed in Table I., although it must be recognized that in so doing we increase somewhat the range of possible fundamental potentials without changing the mean deviations of the computed potentials for the series as a whole. Table II. represents the mean deviation ΔV_0 of the computed potentials for all the elements of Table I, for various arbitrarily chosen values of V_0. It appears that a wide range of fundamental potentials is possible.

TABLE II.

Fundamental Potentials.

Mean V_0.	Mean ΔV_0.	Mean V_0.	Mean ΔV_0.
8.09	±0.25	10.49	±0.23
8.51	0.28	10.85	0.27
9.15	0.28	11.86	0.50
9.45	0.23	12.90	0.50
9.91	0.27		
10.16	0.13		
10.29	0.20		

There is good evidence for believing that the frequency $\nu = 1.5S$ (*or* $1.5\,s$) is an electronic frequency of the type considered by Dr. Allen. Thus experiment, in the case of ionization potential verifies the relation

$h\nu = eV$ where V is the ionizing potential of any metallic vapor and ν is the frequency 1.5 S in the spectrum of this metal. We have then from Dr. Allen's theory, $N\nu = n\nu_0$ where ν_0 represents Rydberg's constant. Whence it would follow that the products of the atomic number and the convergence frequency 1.5 S for the various elements are in the ratio of a series of integral numbers, and that these products $N\nu$ are equal to simple integers multiplied by the value of the Rydberg constant.

These convergence frequencies are known with very considerable accuracy for a number of elements and hence should afford a precise criterion as to the applicability of Dr. Allen's theory. If we denote by ν' the wave-number we have $\nu' = n\nu_0'/N$. The following table gives the values of the wave-number ν' corresponding to the frequency $\nu = 1.5\ S$ for a series of elements. The numbers are supposedly correct to four or five significant figures. The second column gives the corresponding wave-lengths, the sixth column the best value of the integer $n = N\nu'/\nu_0'$ where ν_0' is Rydberg's wave-number, 109679, the seventh column the convergence wave-lengths, λ, computed on the basis of Dr. Allen's theory, and the last column, the differences between the computed and correct values of λ.

TABLE III.

Convergence Frequencies ($\nu = 1.5S$).

Element.	λ $\nu=1.5S$ or $1.5s$.	Wave Number ν'.	N.	$N\nu'$.	Best Value of n.	Computed λ $= \frac{N\cdot 10^8}{N\nu_0'}$.	±(λcomputed —λcorrect).
Na......	2412.6Å	41449	11	455940	4	2507.3	94.7Å
K.......	2856.6	35006	19	665110	6	2887.2	30.6
Mg......	1621.7	61664	12	739970	7	1563.0	58.7
Ca......	2028.2	49305	20	986100	9	2026.1	2.1
Sr.......	2177.5	45924	38	1745100	16	2165.4	12.1
Zn......	1320.0	75760	30	2272800	21	1302.4	17.6
Cd......	1378.7	72533	48	3481600	32	1367.6	11.1
Hg......	1188.0	84176	80	6734100	61	1195.7	7.7

The differences between the computed and correct values of λ are many times greater than the error possible in the determination of λ by use of spectroscopic data. These differences could be reduced somewhat by introducing fractional terms in n such as one fourth, one half and three fourths, but even then the discrepancies are far too large. Furthermore the results do not appear to be improved by choosing a fundamental frequency other than the Rydberg constant. Fundamental frequencies having the values $(2.44, 2.68, 2.94, 3.29, 3.66)\cdot 10^{15}$ satisfy the relation proposed by Dr. Allen almost equally well, but no value of the fundamental frequency appears to represent the data with sufficient accuracy.

It is of interest to consider the theory of Dr. Allen when applied to a series of numbers selected at random, in which there can be no physical significance whatever. The first four columns of Table IV. are taken from one of Dr. Allen's papers. The average deviation ΔV_0 from mean value V_0 chosen by Dr. Allen is ± 0.6 volt. Column 5 of this table contains the same numbers as those given in column 3 but the arrangement is by random distribution obtained by drawing the numbers purely by chance. It is seen that the product NV for this method of grouping can be represented by nV_0, where $V_0 = 7.5$ volts, with a numerical average deviation, ΔV_0, one sixth of that obtained when the numbers are properly arranged. The fact that a random distribution of numbers gives a more accurate law than the correct distribution of the *same* numbers must appeal as an argument against the physical significance of the theory.

Table IV.

Ionization Potentials and Numbers Selected at Random.

Element.	N.	V Allen's Values.	nV.	V Random Values.	nV_0.
H.......	1	11.0	1·11.0	7.5	1·7.5
He......	2	20.5	3·13.7	12.0	3·8.0
N.......	7	7.5	4·13.1	16.0	15·7.5
O.......	8	9.0	5·14.4	11.0	12·7.3
Ne......	10	16.0	12·13.3	4.9	6½·7.5
A.......	18	12.0	16·13.5	20.5	49·7.5
Hg......	80	4.9	30·13.1	9.0	96·7.5
			Mean $V_0 = 13.1$ Mean $\Delta V_0 = \pm 0.6$		Mean $V_0 = 7.5$ Mean $\Delta V_0 = \pm 0.1$

It is of still further interest to apply the same methods used in obtaining the results given in Table I. to a random distribution of the numbers appearing in column 3. This has been done in Table V. The third column of this table contains the same numbers as the third column of Table I., but in Table V. these numbers were arranged by drawing at random. As seen from column 4, the mean factor V_0 is 12.09 volts, and the average deviation, ΔV_0, is ± 0.15 volt, practically the same average deviation obtained in Table I. where the numbers were grouped properly. The pertinence of this illustration is further emphasized by the fact that if the small numbers alone of the two tables are compared, the results are more favorable for the data grouped at random.

TABLE V.

The Same Numbers as Those Appearing in Table I. Grouped at Random.

N.	*V.*	*NV.*	$n \cdot V_0$.	ΔV_0.
1	12	12	1·12.00	.09
2	6.08	12.16	1·12.16	.07
7	5.11	35.77	3·11.92	.17
11	1.60	17.6	1½·11.73	.36
8	5.67	45.4	3¾·12.11	.02
19	3.79	72.0	6·12.00	.09
12	10	120	10·12.00	.09
20	4.9	98	8·12.25	.16
16	2.10	33.6	2¾·12.22	.13
17	5.12	87.0	7·12.43	.34
10	7.5	75	6·12.50	.41
18	2.68	48.2	4·12.05	.04
38	9.1	346.	29·11.93	.16
30	4.02	120.6	10·12.06	.03
56	8.3	465	39·11.92	.17
35	9.35	327	27·12.11	.02
48	8.2	394	33·11.94	.15
80	10.5	840	70·12.00	.09
11	20.2	222	18·12.33	.24
19	10.4	198	16·12.37	.28
12	16	192	16·12.00	.09
30	7.61	228	19·12.00	.09
48	4.32	207	17·12.18	.09
80	8.95	716	60·11.93	.16
			Mean 12.09	±0.15

A further complication in Dr. Allen's theory is that the fundamental integers obtained are not universally fundamental but depend upon the type of electronic or atomic frequency under consideration. Thus, in the case of sodium we find n equals 5½ for ionization potential, 4 for the convergence frequency $\nu = 1.5s$, 2¼ for resonance potential, 2 for the photoelectric limiting frequency, 3 for the maximum of the photoelectric effect, 2¼ for atomic frequency by Lindemann's formula, 1½ by Einstein's formula, 2 by Alterhun's formula, and 2 by specific heat determinations. Since many of the above phenomena are of the same type from the standpoint of the atomic agitation we would expect a closer agreement or at least some simple relation between these integers. Still further there does not appear to be any simple relation between n and the atomic number N, for a series of elements, even when the same phenomenon is considered, as is evident from a comparison of the values given in Table I.

Summary.—The empirical relation proposed by Dr. Allen connecting atomic numbers, fundamental frequencies, fundamental numerals, and ionization potentials does not appear to accurately interpret recent experimental data. The apparent agreement obtained between observed ionization potentials and those computed on the basis of Dr. Allen's theory is due to the fact, the possibility of which was suggested by Dr. Allen, that one is concerned mainly with large numbers, and that sufficiently accurate data are lacking for the three or four elements which would give small enough numbers to afford a criterion of the theory. From an empirical standpoint the theory does not appear to be justified because a wide range of numbers may be chosen for the fundamental frequency with equally satisfactory results.

Also, the theory may be apparently evolved equally well from experimental data arranged properly, or from the same numerical data arranged by chance with no reference to their physical significance. The theory fails in determining the limiting frequencies ($\nu = 1.5S$) of the elements for which these values are accurately known. One might expect the theory to be of value in predicting results which could be more accurately confirmed by experiment. Such is not the case, however. For example, the ionization potential of sodium (or any other material) can not be predicted by this theory because the theory requires a knowledge of the integral multiplier for the ionization potential of sodium which in turn requires a knowledge of the ionization potential for its determination. The integral multipliers for the same element are different for different phenomena and no relation is apparent between the integers determined by different phenomena. In conclusion the writer desires to express his appreciation for the valuable criticism of Dr. W. F. G. Swann in the preparation of the manuscript.

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