

CRITICAL EXAMINATION OF THE LAW OF X-RAY LINE  
SPECTRA.

BY HORACE SCUDDER UHLER.

THE present paper differs from my earlier one<sup>1</sup> on the same subject in three respects: (i) It includes the wave-lengths of all the accurately measured lines of the *K*-series (only a few of which were formerly accessible to me), (ii) it contains the results of more rigorous calculations, and (iii) it presents the material in greater detail. The object of the paper is to subject to critical examination the functional dependence of the *X*-ray lines of any one sub-series upon the corresponding atomic numbers so that answers may be given to the following questions, which are: How accurately does Moseley's law reproduce the observed wave-lengths? What other empirical formula will represent the numerical data within the given limits of experimental error? And what is the probable order of magnitude of the high frequency radiations of elements having small atomic numbers and of which the spectra have not yet been obtained? All the wave-lengths used (save two) may be found in a paper<sup>2</sup> by M. Siegbahn entitled "Bericht über die Röntgenspektren der chemischen Elemente (Experimentelle Methoden und Ergebnisse)." These data were chosen because they are the most recent, they were all obtained in the same laboratory with the same spectrometers, and they constitute the most extensive, accurate, and consistent set available.

In Moseley's second paper<sup>3</sup> the analytical result of his investigations is concisely stated in the sentence: "From the approximate linear relation between  $\nu^{1/2}$  and  $N$  for each line we obtain the general equation  $\nu = A(N - b)^2$ , where  $A$  and  $b$  are constants characteristic of each line." That  $b$  may not equal zero is pointed out very clearly in Moseley's reply<sup>4</sup> to certain objections raised by F. A. Lindemann. Accordingly, in the present paper, the equation  $\sqrt{\nu_N} = a + bN$  will be referred to as Moseley's law. The degree of accuracy with which this relation represents the experimental wave-lengths will now be considered.

<sup>1</sup> Proc. Natl. Acad., Vol. 3, p. 88, Feb., 1917.

<sup>2</sup> Jahrbuch der Radioaktivität und Elektronik, Vol. 13, Part 3, Sept., 1916.

<sup>3</sup> Phil. Mag., Vol. 27, p. 712, April, 1914.

<sup>4</sup> Nature, Vol. 92, p. 554, Jan. 15, 1914.

The values of the parameters  $a$  and  $b$  were calculated, by the method of least squares, from the square-roots of the reciprocals of the known wave-lengths (expressed in angstroms) and the corresponding atomic numbers,  $N$ . Then, from  $a$ ,  $b$ , and  $N$ , the wave-lengths were recalculated.

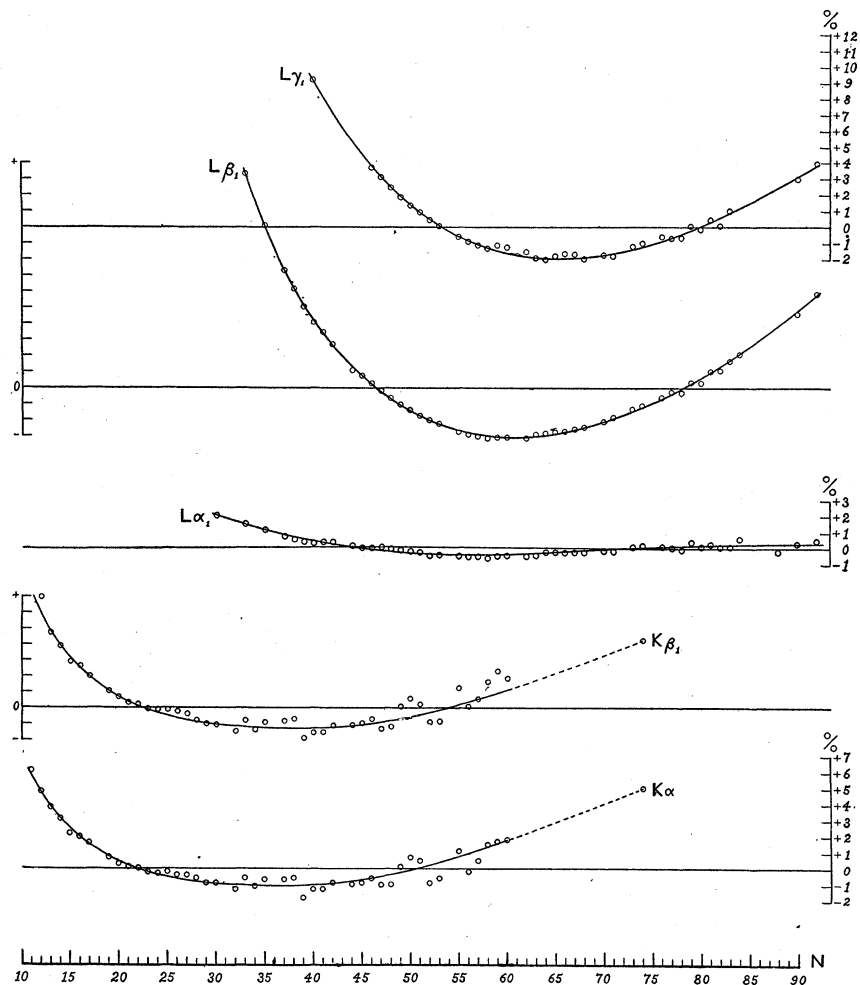


Fig. 1.

Finally the percentages by which the mathematical wave-lengths are algebraically greater than the experimental data were computed. This procedure was followed for the entire experimental range of each of the series  $K-\alpha_m$ ,  $K-\beta_1$ ,  $L-\alpha_1$ ,  $L-\beta_1$ , and  $L-\gamma_1$ . Since some of the lines of the  $K-\alpha$  series have not been measurably resolved into the two components

$\alpha_1$  and  $\alpha_2$ , mean values were used for all of the resolved pairs. For this reason the subscript  $m$  is written below the first  $\alpha$ . The results obtained are shown graphically for five series in Fig. 1, and numerically for the  $K\text{-}\alpha_m$  and  $L\text{-}\beta_1$  series in the columns headed  $\%$ ,  $M$  of Tables I and II. The ordinates (with respect to the corresponding horizontal axes) of the centers of the little circles in the figure are the percentage deviations defined above, the common scale of the diagrams being indicated on the associated vertical axes. The abscissæ of these centers, which represent the atomic numbers, have their scale indicated at the bottom of the figure. The curves drawn through the five sets of points were not obtained by calculation since they are only intended to afford general guides to the eye. The two points at the extreme right ends of the curves for the  $K$  series were plotted from wavelengths for tungsten, kindly furnished by A. W. Hull in a private communication. These data were not used in computing the values of the parameters  $a$  and  $b$  of Moseley's formula. For this reason the curves are indicated by short dashes from  $N = 60$  to  $N = 74$ . Notwithstanding the fact that there is much room for improvement in the portions of the curves pertaining to values of  $N$  greater than 50 (especially for  $K\text{-}\beta_1$ ), nevertheless the two points for tungsten seem to accord very well with the general drift of the nearer points which were derived from Siegbahn's tables. Incidentally, the circles for the  $K\text{-}\alpha_m$  and  $K\text{-}\beta_1$  series show (with the single exception for  $N = 59$ ) precisely the same irregularities of distribution or "accidental" errors. This may indicate that homologous wave-lengths were derived from the same spectrograms and were dependent upon some poorly determined reference line, such as the direct image, for example.

Even a casual inspection of the five graphs brings out the fact that, in general, Moseley's law does not represent at all well the experimental data throughout the entire ranges now at our disposal. The percentage deviations at the extreme points and at the algebraic minima being respectively about + 6, + 5, - 1; + 7, + 4, - 1.2; + 2, + 0.2, - 0.6; + 13.3, + 5.8, - 3; and + 9.2, + 4, - 2; for the  $K\text{-}\alpha_m$ ,  $K\text{-}\beta_1$ ,  $L\text{-}\alpha_1$ ,  $L\text{-}\beta_1$ , and  $L\text{-}\gamma_1$  series. Most of these deviations greatly exceed the experimental errors estimated by the original investigators. For the  $K$  series, from germanium to chromium, it is stated<sup>1</sup> that: "The agreement of the lines measured on different plates is very good; the deviations are of the order of magnitude of 0.1 to 0.2 per cent." For the  $L$  series, from tantalum to uranium, it is remarked<sup>2</sup> that: "The accuracy of the

<sup>1</sup> Physikal. Ztschr., p. 48, Feb. 15, 1916.

<sup>2</sup> Phil. Mag., Vol. 32, p. 41, July, 1916.

measurements is estimated to about 0.3 per cent." With regard to the *L* series, from zinc to lutetium, the author says:<sup>1</sup> "The reflexion angles calculated have an uncertainty of about 0.3 per cent." Unfortunately I have not been able to find data of this kind for the remaining wave-lengths in Siegbahn's list. Hull's values for tungsten, which were obtained by the ionization method, are probably not in error by more than one per cent. Another fact brought out by the graphs is that Moseley's law represents the *L*- $\alpha_1$  series better than any of the remaining four. This is quite contrary to all the accessible statements in the literature of the subject since they consistently convey the impression that Moseley's law holds very well for the *K* series but that it needs correction in the region of shortest wave-lengths of the *L* series. In fact, O. W. Richardson exceeds the original qualifying remarks of Moseley when he says:<sup>2</sup> "For the *K* series the agreement is quite exact, but for the *L* series there is a slight deviation from linearity with the elements of very high atomic weight." Since the preceding examination shows conclusively that Moseley's law (as distinguished from his epoch-making association of the chemical elements with atomic numbers and broad point of view) does not satisfactorily represent the experimental wave-lengths over the entire ranges of the five longest sub-series, the next problem is to find a function which will reproduce the numerical data within the estimated limits of experimental error.

The only interpolation formula which I have been able to find in the literature is the one proposed by A. W. Hull.<sup>3</sup> For the *K* series he gives  $\nu_\alpha = 1.64 \times 10^{15} N^{2.10}$  and  $\nu_\beta = 1.56 \times 10^{15} N^{2.15}$ , true frequencies being represented. Since the exponents of *N* do not seem to be promising from the theoretical standpoint, as their values were obtained by the graphical method alone, and since the formula was not given the more crucial test of the *L* series, I have not subjected it to examination by the method of least squares. On the other hand, Hull's function has at least one desirable property, that is, simplicity.

Since last fall I have tested the equation<sup>1</sup>

$$\sqrt{\nu_N} = A + BN + \frac{C}{D - N} \quad (1)$$

fairly exhaustively without succeeding either in replacing it by a function involving less than four parameters or in finding any systematic deviation between the wave-lengths computed from it and the experimental data. Any true but slight discordance may, of course, be masked by the

<sup>1</sup> Phil. Mag., Vol. 32, p. 497, Nov., 1916.

<sup>2</sup> "The Electron Theory of Matter," p. 511, 1914.

<sup>3</sup> Proc. Natl. Acad., Vol. 2, p. 267, May, 1916.

inaccuracies in the observed quantities, which is a question that future investigation alone can decide. The particular form of equation (1) was found in the following empirical manner. The residuals of  $\sqrt{\nu_N}$  (not percentage deviations of wave-lengths), obtained by applying the method of least squares to Moseley's law, were plotted on a large scale in the hope of obtaining a correction "term" to the linear relation. Inspection of the five sets of points thus obtained suggested that the hyperbola  $c_0N^2 + Nr + c_1N + c_2r + c_3 = 0$  ( $r \equiv$  residual) would fulfil the requirements of the problem. As stated above, subsequent rigorous calculations have confirmed this belief. The correction expression may be transformed into

$$-r = a' + c_0N + \frac{C}{D - N},$$

where  $a' = c_1 - c_0c_2$ ,  $C = c_2(c_1 - c_0c_2) - c_3$ , and  $D = -c_2$ . Since  $\sqrt{\nu_N} = a + bN - r$  the final form is equation (1), where  $A = a + a'$ , and  $B = b + c_0$ . Since equation (1) may be written  $BN^2 - N\sqrt{\nu_N} + (A - BD)N + D\sqrt{\nu_N} - (C + AD) = 0$  the geometric meaning of the new formula is that the square-roots of the frequencies of the X-ray lines are related to the atomic numbers in the same way as the ordinates and abscissæ of the points on an hyperbola. In short, these radicals form a family of hyperbolæ for the five series tested. This result was brought out by the magnification of which the residuals were susceptible, but it could not have been seen so readily by plotting  $\sqrt{\nu_N}$  against  $N$  directly. See, for example, the approximate straight lines given by Moseley, Siegbahn, and others.

The wave-lengths calculated by the aid of formula (1) and the percentage deviations of the numbers thus obtained are given in the columns headed  $\lambda_e$ ,  $U$  and  $\%$ ,  $U$ , respectively, in Tables I and II. The series  $K\text{-}\alpha_m$  and  $K\text{-}\beta_1$  were selected as typical since the shorter wave-lengths of the former seem to involve relatively large experimental errors while those of the latter appear to constitute the most accurate set of all. For the same reasons the correction coefficients  $c_0$ ,  $c_1$ ,  $c_2$ ,  $c_3$  were obtained graphically for the  $K\text{-}\alpha_m$  series, and by the method of least squares for the  $L\text{-}\beta_1$  lines. In fact, as might be expected, in the cases where both methods were applied to one and the same series the gain in accuracy attained by the more rigorous computation was slight and altogether incommensurate to the extra labor entailed. The probable errors of a single residual, expressed in per cent., are  $\pm 0.28$ ,  $\pm 0.25$ ,  $\pm 0.11$ ,  $\pm 0.10$ , and  $\pm 0.16$  for the  $K\text{-}\alpha_m$ ,  $K\text{-}\beta_1$ ,  $L\text{-}\alpha_1$ ,  $L\text{-}\beta_1$ , and  $L\text{-}\gamma_1$  series, in the order named. It is therefore clear that equation (1) represents the

TABLE I.

*Series K- $\alpha_m$ .*

El.	<i>N.</i>	$\lambda_e$	$\lambda_e, M.$	$\lambda_e, U.$	$\%, M.$	$\%, U.$
W.....	74	0.210	0.220	0.210	+5.0	0.0
Nd.....	60	0.333	0.338	0.334	+1.8	+0.3
Pr.....	59	0.345	0.350	0.346	+1.7	+0.4
Ce.....	58	0.358	0.363	0.359	+1.5	+0.4
La.....	57	0.374	0.376	0.373	+0.5	-0.4
Ba.....	56	0.391	0.390	0.387	-0.2	-0.9
Cs.....	55	0.400	0.405	0.402	+1.1	+0.5
I.....	53	0.439	0.437	0.435	-0.6	-0.9
Te.....	52	0.458	0.454	0.453	-0.9	-1.0
Sb.....	51	0.470	0.472	0.472	+0.5	+0.5
Sn.....	50	0.489	0.492	0.493	+0.7	+0.8
In.....	49	0.513	0.513	0.514	+0.1	+0.3
Cd.....	48	0.541	0.535	0.537	-1.0	-0.7
Ag.....	47	0.565	0.559	0.561	-1.0	-0.6
Pd.....	46	0.588	0.584	0.587	-0.6	-0.1
Rh.....	45	0.617	0.612	0.615	-0.9	-0.3
Ru.....	44	0.647	0.641	0.645	-1.0	-0.3
Mo.....	42	0.712	0.705	0.711	-0.9	-0.1
Nb.....	41	0.752	0.741	0.748	-1.3	-0.5
Zr.....	40	0.791	0.780	0.788	-1.3	-0.3
Y.....	39	0.838	0.822	0.831	-1.8	-0.8
Sr.....	38	0.874	0.868	0.877	-0.6	+0.4
Rb.....	37	0.924	0.918	0.927	-0.7	+0.4
Br.....	35	1.038	1.030	1.042	-0.7	+0.4
Se.....	34	1.107	1.094	1.107	-1.1	0.0
As.....	33	1.172	1.165	1.178	-0.6	+0.5
Ge.....	32	1.259	1.242	1.256	-1.3	-0.2
Zn.....	30	1.435	1.422	1.437	-0.9	+0.1
Cu.....	29	1.541	1.527	1.542	-0.9	+0.1
Ni.....	28	1.655	1.645	1.660	-0.6	+0.3
Co.....	27	1.783	1.776	1.791	-0.4	+0.4
Fe.....	26	1.930	1.923	1.937	-0.4	+0.4
Mn.....	25	2.095	2.090	2.103	-0.2	+0.4
Cr.....	24	2.286	2.279	2.290	-0.3	+0.2
V.....	23	2.500	2.495	2.503	-0.2	+0.1
Ti.....	22	2.744	2.744	2.747	0.0	+0.1
Sc.....	21	3.030	3.032	3.029	+0.1	0.0
Ca.....	20	3.357	3.367	3.355	+0.3	-0.1
K.....	19	3.737	3.761	3.737	+0.7	0.0
Cl.....	17	4.712	4.790	4.723	+1.6	+0.2
S.....	16	5.360	5.470	5.369	+2.0	+0.2
P.....	15	6.168	6.306	6.155	+2.2	-0.2
Si.....	14	7.131	7.349	7.127	+3.1	-0.1
Al.....	13	8.360	8.675	8.347	+3.8	-0.2
Mg.....	12	9.915	10.394	9.909	+4.8	-0.1
Na.....	11	11.951	12.681	11.951	+6.1	0.0

TABLE II.

Series  $L\beta_1$ .

El.	$N$ .	$\lambda_e$ .	$\lambda_e, M$ .	$\lambda_e, U$ .	% $M$ .	% $U$ .
U.....	92	0.720	0.762	0.719	+ 5.84	-0.11
Th.....	90	0.766	0.801	0.764	+ 4.62	-0.22
Po.....	84	0.920	0.940	0.921	+ 2.13	+0.11
Bi.....	83	0.950	0.966	0.951	+ 1.69	+0.08
Pb.....	82	0.983	0.994	0.982	+ 1.09	-0.13
Tl.....	81	1.012	1.023	1.014	+ 1.04	+0.19
Hg.....	80	1.049	1.053	1.047	+ 0.35	-0.15
Au.....	79	1.080	1.084	1.082	+ 0.38	+0.21
Pt.....	78	1.120	1.117	1.119	- 0.28	-0.12
Ir.....	77	1.154	1.151	1.157	- 0.23	+0.23
Os.....	76	1.194	1.187	1.196	- 0.56	+0.19
W.....	74	1.278	1.265	1.281	- 1.05	+0.22
Ta.....	73	1.323	1.306	1.326	- 1.28	+0.23
Lu.....	71	1.421	1.395	1.423	- 1.80	+0.12
Yb.....	70	1.474	1.444	1.475	- 2.07	+0.04
Er.....	68	1.586	1.548	1.586	- 2.42	0.00
Ho.....	67	1.646	1.604	1.646	- 2.56	-0.01
Dy.....	66	1.709	1.663	1.709	- 2.67	-0.01
Tb.....	65	1.775	1.726	1.775	- 2.75	0.00
Gd.....	64	1.844	1.793	1.845	- 2.79	+0.04
Eu.....	63	1.918	1.863	1.918	- 2.87	+0.01
Sa.....	62	2.000	1.937	1.996	- 3.13	-0.21
Nd.....	60	2.167	2.101	2.164	- 3.06	-0.14
Pr.....	59	2.259	2.190	2.255	- 3.05	-0.16
Ce.....	58	2.359	2.285	2.352	- 3.12	-0.28
La.....	57	2.461	2.387	2.455	- 3.00	-0.25
Ba.....	56	2.569	2.496	2.564	- 2.86	-0.20
Cs.....	55	2.684	2.612	2.680	- 2.69	-0.16
I.....	53	2.934	2.870	2.934	- 2.19	0.00
Te.....	52	3.074	3.013	3.074	- 1.97	0.00
Sb.....	51	3.222	3.168	3.223	- 1.67	+0.04
Sn.....	50	3.381	3.335	3.383	- 1.36	+0.06
In.....	49	3.550	3.515	3.554	- 0.98	+0.13
Cd.....	48	3.733	3.711	3.738	- 0.59	+0.14
Ag.....	47	3.929	3.923	3.936	- 0.15	+0.17
Pd.....	46	4.142	4.154	4.148	+ 0.29	+0.15
Rh.....	45	4.372	4.406	4.378	+ 0.78	+0.13
Ru.....	44	4.630	4.682	4.625	+ 1.12	-0.10
Mo.....	42	5.175	5.317	5.185	+ 2.74	+0.19
Nb.....	41	5.493	5.684	5.502	+ 3.47	+0.16
Zr.....	40	5.851	6.090	5.847	+ 4.08	-0.07
Y.....	39	6.227	6.542	6.224	+ 5.05	-0.04
Sr.....	38	6.639	7.045	6.638	+ 6.12	-0.02
Rb.....	37	7.091	7.610	7.092	+ 7.31	+0.02
Br.....	35	8.141	8.962	8.146	+10.09	+0.07
As.....	33	9.449	10.710	9.445	+13.35	-0.04

chosen data very satisfactorily and that it will be found very reliable for interpolation, and for extrapolation over a short range of atomic numbers. To facilitate such calculations the numerical values of  $A$ ,  $B$ ,  $C$ , and  $D$  are given in Table III. The column headed "Range" contains the extreme values of  $N$  used in calculating these four coefficients.

In using this table two facts should be noted: (i) Siegbahn used the grating space  $d = 2.814 \times 10^{-8}$  cm. for rock salt, and  $d = 7.621 \times 10^{-8}$  cm. for gypsum; and (ii) the values of  $\lambda_N$  resulting from the use of equation (1) and the tabulated numerical coefficients will be expressed in angstroms.

TABLE III.

Series.	$A$ .	$B$ .	$C$ .	$D$ .	Range.
$K-\alpha$ .....	-0.18724	+0.026898	+ 21.74629	+131.388*	11-74
$K-\beta_1$ .....	-0.44795	+0.027774	+ 69.60474	+170.987	12-74
$L-\alpha_1$ .....	-0.55066	+0.013658	-108.60609	-225.000*	30-92
$L-\beta_1$ .....	-0.43675	+0.009386	+ 66.94285	+180.973	33-92
$L-\gamma_1$ .....	-0.26791	+0.012837	+ 19.38426	+145.197	40-92

\* Obtained by graphical treatment of *residuals*.

Before passing to the question of extrapolating to  $N = 1$  it may not be superfluous to call attention to the following points. In the first place, with the exception of the top number, the values of  $D$  in Table III are approximately integers. Undoubtedly these constants may be replaced by the nearest integers without sensibly decreasing the present accuracy of fit of equation (1), it being at most necessary to apply small corrections to the associated values of  $A$ ,  $B$ , and  $C$ . Since slight changes in the experimental data exert an appreciable influence on  $D$ , and as the value of this constant is very close to an integer for the series  $L-\beta_1$  ( $-0.015$  per cent. error), the wave-lengths of which seem to be affected by the smallest accidental errors, I am still<sup>1</sup> of the opinion that, if the correct formula for  $X$ -ray line series, when found, contains a binomial of the type  $(D - N)^{-n}$ ,  $D$  will be exactly a whole number; signifying, perhaps, a physical change in origin for  $N$ . If this be true, it might be desirable to express  $\nu_N$  as a function of  $D - N$  instead of  $N$  alone. In the second place, realizing that equation (1) possesses the undesirable feature of involving four parameters I tried the formulæ  $\nu_N = a + b(c + N)^{-1}$  and  $\nu_N = a' + b'(c' + N)^{-2}$  which were suggested by the expression obtained by squaring equation (1). It was found that both of the functions just given are altogether unsatisfactory.

An attempt will now be made to arrive at a necessarily tentative answer to the third question proposed in the first paragraph of this paper.



The problem is to determine the order of magnitude of the  $X$ -ray lines of hydrogen by making use only of wave-lengths of the same series and purposely avoiding the introduction of any auxiliary theoretical assumptions. By plotting, on a large scale, atomic numbers and wave-lengths as abscissæ and ordinates respectively it becomes apparent at once that the loci of the five longest series approach the axis of ordinates very gradually as the atomic numbers decrease. Accordingly the wave-lengths deduced for hydrogen may be expected to depend to an undesirable degree upon the particular form of function employed for extrapolation. Especial care must therefore be taken to choose an algebraic expression which will implicitly influence the results to as slight an extent as possible. In spite of the fact that the  $K\text{-}\alpha_m$  series only has to be extrapolated from  $N = 11$  to  $N = 1$ , neither the linear law nor equation (1) will suffice. Moseley<sup>3</sup> assigns to  $b$  [ $\nu_N = A(N - b)^2$ ] the values 1 and 7.4 for the " $K\alpha$  line" and the " $K\beta$  line," respectively. Hence, his formula leads to an infinite wave-length for the  $K\text{-}\alpha_m$  line of hydrogen. For the  $K\text{-}\beta_1$  series the same equation causes  $\lambda_N$  to increase as  $N$  decreases from 11 to 8, to become infinite for  $N = 7.4$ , and to decrease when  $N$  continues from 7 to 1. Siegbahn<sup>6</sup> writes the law in question as  $\sqrt{\nu} = a(N - N_0)$ , and finds that the values of  $N_0$  are 6.97, 6.09, and 9.92 for the interval Ta to U of the  $\alpha_1$ ,  $\alpha_2$ , and  $\beta_2$  sub-series of the  $L$  group. Equation (1) exhibits the same peculiarity, the right member vanishing when  $N$  equals 1.35, 5.88, 11.54, and 9.72 for the series  $K\text{-}\beta_1$ ,  $L\text{-}\alpha_1$ ,  $L\text{-}\beta_1$ , and  $L\text{-}\gamma_1$ , respectively. For the  $K\text{-}\alpha_m$  series and  $N = 1$  it leads to the relatively enormous wave-length  $2.42 \mu$ . A variety of explanations of these apparent anomalies suggest themselves at once. (a) The elements of small atomic number may not radiate the  $K$  and  $L$  series. This idea is consistent with the fact that the  $M$  series has only been found for the elements of high atomic number (79 to 92) from gold to uranium. (b) The  $X$ -ray wave-lengths may pass through arithmetical maxima and then decrease. This would be somewhat analogous to the correlation of the lines of certain principal series in the visible and infra-red regions of the spectrum which correspond to negative values of the frequency in the formula of Ritz. (c) The concordance of formula (1) with the experimental data may be illusory. Although the third suggestion may be the correct one it seems fair to call attention to the fact that the errors involved in the given wave-lengths (especially for the elements of high atomic number) exert an appreciable influence on the values of the parameters  $A$ ,  $B$ ,  $C$ , and  $D$ . Thus, for the  $K\text{-}\alpha_m$  series, substitution of  $N = 1$  in equation (1) leads to  $\sqrt{\nu_1} = -0.1872 + 0.0269 + 0.1668 = 0.0065$  or  $\nu_1 = 0.000042$ .

Slight changes in the coefficients would therefore produce a very great alteration in the wave-length obtained from  $\sqrt{\nu_1} = A + B + C(D - 1)^{-1}$ .

The least objectionable way of extrapolating is to apply the method of least squares to the computation of the coefficients of a sufficient number of terms of the power polynomial  $\nu_N = a_0 + a_1N + a_2N^2 + \dots + a_kN^k$ , care being taken to use about fifteen of the largest wave-lengths. An inspection of the left ends of the five curves of Fig. 1, or reference to the original papers, will show that the data in these regions are fortunately the most accurate. Using only the first three terms of the polynomial and then putting  $N = 1$  leads to 366 Å., 95 Å., and 22 Å. respectively, for the series  $K-\alpha_m$ ,  $L-\alpha_1$ , and  $L-\beta_1$ . Four terms give 130 Å. and 49 Å. for  $K-\alpha_m$  and  $L-\beta_1$ . The corresponding values of  $a_3$  were  $-0.000000698$  and  $+0.000000320$ , and hence further calculations were omitted as superfluous. Accordingly, the evidence obtained solely from the experimental wave-lengths leads to the tentative conclusion that the  $X$ -ray lines for all the elements will have wave-lengths inferior to 510 Å., which is the limit last attained by Lyman. Incidentally it may be noted that, for the  $L-\beta_1$  series, extrapolation to  $N = 92$  (uranium) by aid of the cubic ( $a_0, a_1, a_2, a_3$ ) gives an error of  $+9.6$  per cent. in the calculated wave-length. Therefore, the close fit of formula (1) cannot be due entirely to the fact that it involves four independent parameters.

In conclusion four sentences in Moseley's second paper<sup>3</sup> will be quoted for reasons which will appear later. "On this principle the integer  $N$  for  $Al$ , the thirteenth element, has been taken to be 13, and the values of  $N$  then assumed by the other elements are given on the left-hand side of Fig. 3. This proceeding is justified by the fact that it introduces perfect regularity into the  $X$ -ray spectra." "Now if either the elements were not characterized by these integers, or any mistake had been made in the order chosen or in the number of places left for unknown elements, these regularities would at once disappear. We can therefore conclude from the evidence of the  $X$ -ray spectra alone, without using any theory of atomic structure, that these integers are really characteristic of the elements." The point to be brought out is that the last sentence must not be taken so literally as to mean that the  $X$ -ray data alone necessitate associating the integers 1, 2,  $\dots$ , 13,  $\dots$ , 74,  $\dots$ , 92 with H, He,  $\dots$ , Al,  $\dots$ , W,  $\dots$ , U, respectively; for, the "regularities" will not disappear if the coördinate plane be expanded or contracted parallel to the axis of  $N$ . More specifically, as far as the  $X$ -ray data are concerned, the atomic numbers need not be integral and they do not have to form an arithmetical progression explicitly.<sup>1</sup> In fact, in making the computa-

<sup>1</sup> The discrete values of  $\log N$ , say, may be taken as a new sequence of atomic numbers, thus involving the accepted series implicitly.

tions I shifted the origin to the "center of gravity" of the  $N$  sequence, divided by 10, etc. These comments would be highly pedantic and irrelevant if removed from the following remarks. The facts that equation (1) leads to infinite wave-lengths for values of  $N$  appreciably greater than unity, that the  $M$  series has only been excited in the heaviest elements, and that—as Siegbahn points out—the intensities of the lines of any one sub-series decrease, on the whole, and finally vanish (experimentally) as the atomic number becomes smaller, suggest that the mechanisms which give rise to these radiations may cease to function or even to exist (loss of outer rings of electrons) for definite values of  $N$ . In short, if it should ever become desirable, for theoretical or other reasons, to use different sets of atomic numbers for the  $K$ ,  $L$ , and  $M$  series the transformation of coördinates would not disturb the fundamentally important regularities discovered by Moseley.

## SUMMARY.

1. It is shown that Moseley's law,  $\nu = A(N - b)^2$ , does not satisfactorily represent the  $X$ -ray series over the entire ranges of wave-lengths now known.

2. The formula  $\nu^{1/2} = A + BN + C(D - N)^{-1}$ —where  $A$ ,  $B$ ,  $C$ , and  $D$  are constants for any one sub-series—is proposed and shown to reproduce the observed data within the given limits of experimental error.

3. The uncertainty pertaining to extrapolation of the series as far as hydrogen is discussed. The tentative conclusion is reached that the  $X$ -ray lines of hydrogen, if they exist, probably have wave-lengths less than about 400 angstroms.

4. Attention is called to the fact that the series of natural numbers commencing with 1 is not the only arithmetical progression which may be used as the sequence of atomic numbers consistent with Moseley's "regularities."

SLOANE PHYSICAL LABORATORY,  
YALE UNIVERSITY,  
February 1, 1917.