THE LOGARITHMIC LAW CONNECTING ATOMIC NUMBER AND FREQUENCY DIFFERENCES IN SPECTRAL SERIES.

BY GLADYS A. ANSLOW.

SYNOPSIS.—In continuation of a previous note by Anslow and Howell graphic and algebraic relations are derived between the logarithms of the atomic numbers and of the ν, $\nu_1 + \nu_2$, ν_1 and ν_2 constant frequency differences occurring in the spectral series of alternate members of the same chemical family. Two systems of four approximately straight lines approaching parallelism resulted when a family possessed both doublet and triplet series. The equations derived are of the form $\nu = (N/mnk)^A$, where N is the atomic number of the element; A is a constant depending upon the system; n is an integer, the same for both systems in the same family; k is a constant, 0.080; and m takes on successive integral values for the ν, $\nu_1 + \nu_2$, and ν_1 equations. The agreement between the calculated and observed values of frequency differences indicates that the logarithmic lines should curve upwards for elements of high atomic number. The equations derived and the fact that an approximate linear relation seems to exist between the convergence frequencies of members of the same system of series and their atomic numbers do not seem to follow from the Bohr-Sommerfeld theory of atomic structure as so far developed and indicate that some adjustments to the theory are necessary if it is to be extended to predict optical series.

IN an earlier note Mrs. Janet Howell Clark and the author[1] called attention to an extension of the modified law of Runge and Precht[2] concerning the frequency differences of the doublet and triplet spectral series in a given family of the Mendelejeff chemical series. Ives and Stuhlmann[3] had found by a graphical method that a linear relation exists between the logarithms of the atomic numbers of the elements of one family and the logarithms of their doublet separations. Plotting the logarithms of the atomic numbers of the members of the second chemical family against the logarithms of the sum of the constant frequency differences of the triplets in their spectra, we found that linear relations exist between alternate members of the family, the points for magnesium, zinc, cadmium and mercury lying on one line, and those for calcium, strontium, barium and radium on another.

Bell[4] has recently published a treatise on the relation of atomic number to the doublet and triplet separations in the different chemical families. Testing the relation $\nu = A(N - N_0)^2$, where ν stands for the frequency

[1] Anslow and Howell, Proceedings of the National Academy of Sciences; III., p. 409, 1917.

[2] Runge and Precht, Philosophical Magazine; V., p. 476, 1903.

[3] Ives and Stuhlmann, PHYS. REV., V., p. 368, 1915.

[4] Bell, Philosophical Magazine, XXXVI., p. 337, 1918.

difference, N for the atomic number, and A and N_0 are constants, he finds that such an equation approximately predicts the doublet and triplet separations of the different elements if we assume two such

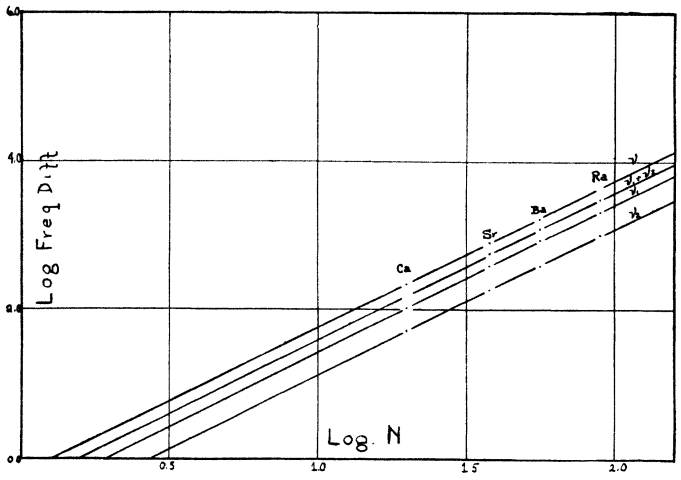

Fig. 1.

equations for each family which branch in the case of the first and second families at potassium and magnesium respectively. He also derives an equation for the logarithmic relation between the same quantities, putting

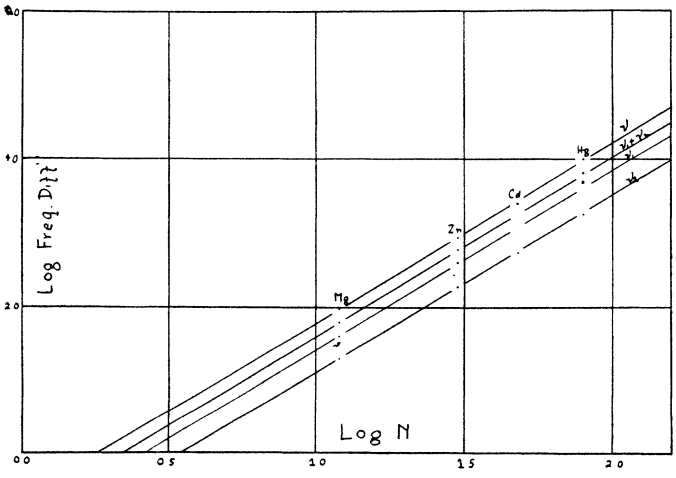

Fig. 2.

the equation in the form, $\log \nu = p \log N + q$, where p and q are constants, but discards such a relation as not an essential improvement

upon the relation $\nu = A(N - N_0)^2$. He also states that "the logarithmic method fails to show graphically the branching relation of the columns."

However, the plotting of the logarithmic equations does show the existence of two equations for each family as is evident from the diagrams in the article by Mrs. Clark and myself, where we attempted to make this fact clear. It happens that I had calculated the equations of the logarithmic lines for the different families where series are known and since the form in which I stated my final results is slightly different from Mr. Bell's, it shows some interesting relationships.

Since the spectral series of the elements in the second chemical family have been the most fully worked out for any family, I will consider it first. I have plotted the logarithms of the doublet separation, ν, and of the triplet separations ν_1, ν_2, and $\nu_1 + \nu_2$ against the logarithms of the

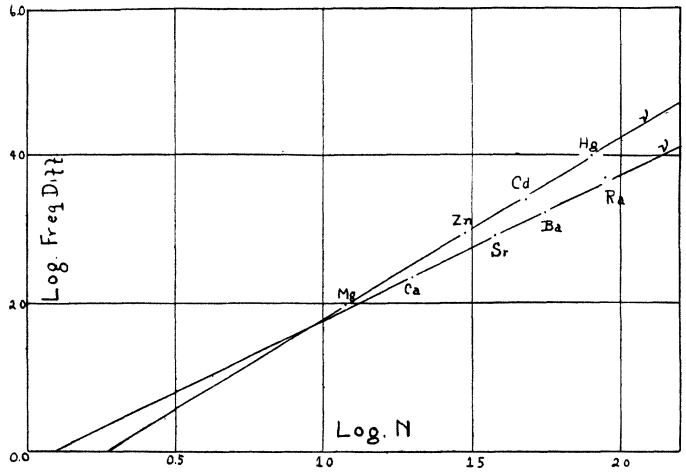

Fig. 3.

atomic numbers of the elements and have obtained lines which pass through Ca, Sr, Ba and Ra (Fig. 1), and through Mg, Zn, Cd and Hg (Fig. 2). The striking feature of the result is that the lines for each system are approximately parallel. If the two systems are plotted on the same diagram, corresponding lines will intersect at points slightly below those for magnesium. This fact is shown for the ν lines in Fig. 3. The equations of the lines were first put into the form,

$$\log \nu = A(\log N - C)$$

and this equation then solved into $\nu = (N/B)^A$, where B = antilog. C. The constants A and B which appear in the mean equations of the lines are tabulated below.

The values for the frequency differences are taken, for the sake of comparison, the same as those taken by Bell and given by Dunz.[1] The values for the radium triplets are those given in our earlier paper. It should be noticed that the triplet differences 2050 and 832 found by Hicks[2] fit almost as well into the equations derived. Values marked * were not used in the calculation of the formulæ.

TABLE I.

Element.	N.	ν Obs.	ν Calc.	ν Calc.$-\nu$ Obs.	$\nu_1+\nu_2$ Obs.	$\nu_1+\nu_2$ Calc.	$\nu_1+\nu_2$ Calc. $-\nu_1+\nu_2$ Obs.
Ca.....	20	222.9	225.6	+ 2.7	158.10	159.8	+ 1.7
Sr.....	38	801.3	795.8	− 5.5	581.49	578.0	+ 3.5
Ba.....	56	1690.5	1704.6	+ 14.1	1248.7	1255.6	+ 6.9
Ra.....	88	4858.0*	4140.9	−717.1	3052.7*	3103.9	+ 51.2
	A = 1.964				A = 2.002		
	B = 1.267 = 4 × .317				B = 1.586 = 5 × .317		
Element.	N.	ν_1 Obs.	ν_1 Calc.	ν_1 Calc. $-\nu_1$ Obs.	ν_2 Obs.	ν_2 Calc.	ν_2 Calc. $-\nu_2$ Obs.
Ca.....	20	105.99	105.5	− 0.5	52.11	52.1	+ 0.0
Sr.....	38	394.44	394.7	+ 0.3	187.05	187.0	+ 0.0
Ba.....	56	878.4	875.6	− 2.8	370.3*	408.4	+ 38.1
Ra.....	88	2016.6*	2216.6	+200.0	1036.1*	1005.8	− 30.3
	A = 2.055				A = 1.994		
	B = 2.072 = 6 × .345				B = 2.747		
Element.	N.	ν Obs.	ν Calc.	ν Calc. $-\nu$ Obs.	$\nu_1+\nu_2$ Obs.	$\nu_1+\nu_2$ Calc.	$\nu_1+\nu_2$ Calc. $-\nu_1+\nu_2$ Obs.
Mg.....	12	92.0	91.4	− 0.6	60.86	61.0	+ 0.1
Zn.....	30	872.4	872.6	+ 0.2	578.79	578.1	− 0.8
Cd.....	48	2484.1*	2776.4	+312.3	1712.91*	1831.7	+118.8
Hg.....	80	9835.06	9766.2	− 68.9	6397.50	6412.2	+ 14.7
	A = 2.462				A = 2.454		
	B = 1.917 = 6 × .319				B = 2.247 = 7 × .321		
Element.	N.	ν_1 Obs.	ν_1 Calc.	ν_1 Calc. $-\nu_1$ Obs.	ν_2 Obs.	ν_2 Calc.	ν_2 Calc. $-\nu_2$ Obs.
Mg.....	12	40.95	40.9	+ 0.0	19.89	19.9	+ 0.0
Zn.....	30	388.91	388.9	+ 0.0	189.78	189.8	+ 0.0
Cd.....	48	1171.05*	1234.1	+ 63.0	541.86*	604.2	+ 63.3
Hg.....	80	4630.31*	4328.4	−301.9	1767.19*	2127.0	+359.8
	A = 2.457				A = 2.462		
	B = 2.648 = 8 × .331				B = 3.560		

The equations derived show that A is approximately constant for each system, as is to be expected since the plotted lines approach parallelism. Moreover, the constants B for the ν, $\nu_1 + \nu_2$ and ν_1 lines of

[1] Dunz, Bearbeitung unserer Kentnisse von der Serien, Tubingen, 1911.

[2] Hicks, Philosophical Transactions, A, CCXIL., 33.

both systems are successive integral multiples of the same factor, 0.32. The agreement between the observed and calculated values for the separations is fairly good for elements of low atomic number, but poor for those elements which lie beyond the rare earths in the chemical series. The differences between the values found for cadmium seem to indicate that either the series used are not related to those with which they are commonly supposed to be similar to in other elements, or the structure of the atom of this element is not exactly similar to that of the other elements in the same group, so that it acts as if its atomic number were less than that which has been assigned to it. Attention is also called to the fact that much better values could be calculated for the ν_1 separations of radium and mercury if the values of B were more nearly equal to $6 \times .320$ and $8 \times .320$, respectively.

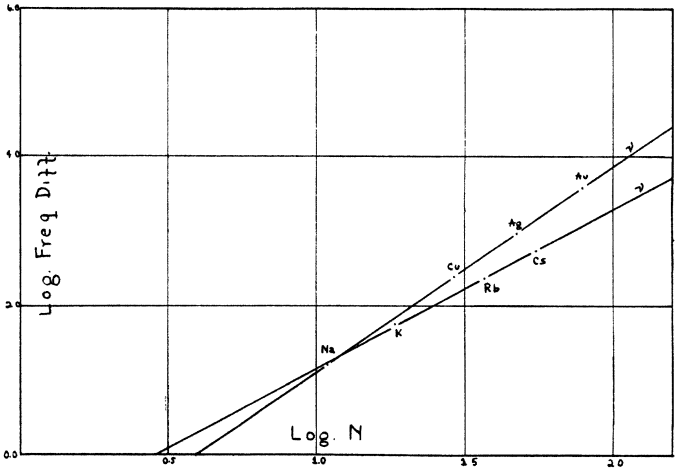

Fig. 4.

Since alternate elements are related in this way, it should be possible to predict frequency differences in elements where they are not yet known. The lines through Ca, Sr, Ba and Ra predict the separations $\nu = 9.56$; $\nu_1 + \nu_2 = 6.95$; $\nu_1 = 3.91$; and $\nu_2 = 2.17$ for beryllium. The spectrum shows the differences 8.9, 6.8, 4.1 and 2.5 between lines which occur in pairs, but not in triplets. A magnetic study of the lines in question has been made by Popow[1] proving that they belong to doublet and triplet series. Possibly the simplicity of the atom prevents the appearance of the three lines in the spectrum at once, but permits doublets with the separations corresponding to the triplet separations.

The results for Group 1 are plotted in Fig. 4 and the equations derived

[1] Popow, Verhandlungen der Schweizerischen Naturforschenden Gesellschaft, Sept., 1913.

are shown in Table II. In this group only the doublet series have been discovered with the exception of copper.

TABLE II.

Element.	N.	ν Obs.	ν Calc.	ν Calc. $-\nu$ Obs.	Element.	N.	ν Obs.	ν Calc.	ν Calc. $-\nu$ Obs.
Na.....	11	17.21	17.21	+0.0	Li.....	3	0.34*	1.09	+0.7
Cu.....	29	248.13*	245.4	−2.7	K.....	19	57.90	57.1	−0.8
Ag.....	48	920.56	922.0	+1.4	Rb.....	37	237.71	239.0	+1.3
Au.....	79	3817.20	3826.7	+9.5	Cs.....	55	564.10	559.7	−4.4
$A = 2.741$					$A = 2.147$				
$B = 3.895 = 8 \times .486$					$B = 2.887 = 6 \times .481$				

As in Group 2 two values appear for A, and B is seen to be an integral multiple of the constant, 0.483. If the behavior of the light emitting electrons of the two families is similar, we should expect the appearance of triplet series in this group, and the equations which should predict the values of $\nu_1 + \nu_2$ and ν_1 are for Na, Cu, Ag and Au

$$\nu_1 + \nu_2 = \left(\frac{N}{9 \times .483}\right)^{2.741}$$

and

$$\nu_1 = \left(\frac{N}{10 \times .483}\right)^{2.741};$$

and for Li, K, Rb and Cs

$$\nu_1 + \nu_2 = \left(\frac{N}{7 \times .483}\right)^{2.147}$$

and

$$\nu_1 = \left(\frac{N}{8 \times .483}\right)^{2.147}.$$

Two systems of triplets have been discovered in the spectrum of copper by Rydberg[1] with the separations $\nu_1 + \nu_2 = 129.50 + 50.58 = 180.08$; and $680.10 + 212.21 = 892.41$. Assuming that A should have the same value for these triplets as for the doublets the values derived for B are

$B^{\nu_1+\nu_2}$,	$4.324 = 9 \times .481$;	$2.432 = 10 \times .243$
B^{ν_1},	$4.918 = 10 \times .491$;	$2.685 = 11 \times .244$
B^{ν_2},	6.728	4.102

The agreement between the predicted values for B and those derived from the triplets with the smaller frequency differences is striking, the other system of triplets being, apparently, a secondary one with B a

[1] Rydberg, Astrophysical Journal, VI., p. 239, 1897.

multiple of a constant half as large as for the other. These results support the hypothesis that the graphs for the ν, $\nu_1 + \nu_2$, ν_1, and ν_2 separations in Figs. 1 and 2 are parallel straight lines.

If the latter three lines are parallel, the following equations can be stated for the triplets in any element

$$\nu_1 + \nu_2 = \left(\frac{N}{B_{\nu_1+\nu_2}}\right)^A \tag{1}$$

$$\nu_1 = \left(\frac{N}{B_{\nu_1}}\right)^A \tag{2}$$

$$\nu_2 = \left(\frac{N}{B_{\nu_2}}\right)^A \tag{3}$$

and subtracting (2) from (1)

$$\nu_2 = (N)^A\left[\left(\frac{1}{B_{\nu_1+\nu_2}}\right)^A - \left(\frac{1}{B_{\nu_1}}\right)^A\right] \tag{4}$$

which leads to the following relation between the constants,

$$\left[\left(\frac{1}{B_{\nu_1+\nu_2}}\right)^A - \left(\frac{1}{B_{\nu_1}}\right)^A\right]^{1/A} = \frac{1}{B_{\nu_2}}. \tag{5}$$

I have tested this result for the triplets considered. The ν_1 value for A for Ca, Sr, Ba, and Ra is so different from those for $\nu_1 + \nu_2$ and ν_1 that I have calculated second values for B from the Ca, Sr and Ba ν_1 separations, and from the Ca and Sr ν_2 separations, assuming $A = 2.002$, which is that derived for the $\nu_1 + \nu_2$ separations. The results are placed below those taken from Table I.

TABLE III.

System.	$B_{\nu_1+\nu_2}$.	B_{ν_1}.	$[(B^{-1}_{\nu_1+\nu_2})^A - (B^{-1}_{\nu_1})^A]^{-1/A}$.	B_{ν_2}.	$d(B_\nu)$.
Ca, Sr, Ba, Ra....	1.586	2.054	2.494	2.746	0.252
Ca, Sr, Ba, Ra....		1.922	2.800	2.780	0.020
Mg, Zn, Cd, Hg...	2.247	2.648	3.543	3.560	0.017
Cu.....	4.324	4.918	6.728	6.930	0.202
Cu.....	2.432	2.685	4.102	4.108	0.006

The values in the last column give the differences between the two calculated values of B_{ν_2}, and are so small that the hypothesis of parallelism between the series separations is strengthened.

Triplets appear again in Group VI., and have been discovered in the spectra of O, S and Se (Fig. 5). If the alternate members in this group are spectroscopically related those in O should not be related to those in

S and Se, but to the undiscovered triplets in Cr, Mo, W and U. From the separations $\nu_1 + \nu_2 = 18.15 + 11.13 = 29.16$ in S, and $\nu_1 + \nu_2 = 103.7 + 44.07 = 148.48$ in Se, the following equation is derived.

$$\nu_1 + \nu_2 = \left(\frac{N}{3.356}\right)^{2.160} = \left(\frac{N}{7 \times .479}\right)^{2.160}.$$

The similarity between this equation and the one predicted for the undiscovered triplets of Li, K, Rb and Cs is apparent. If they are identical

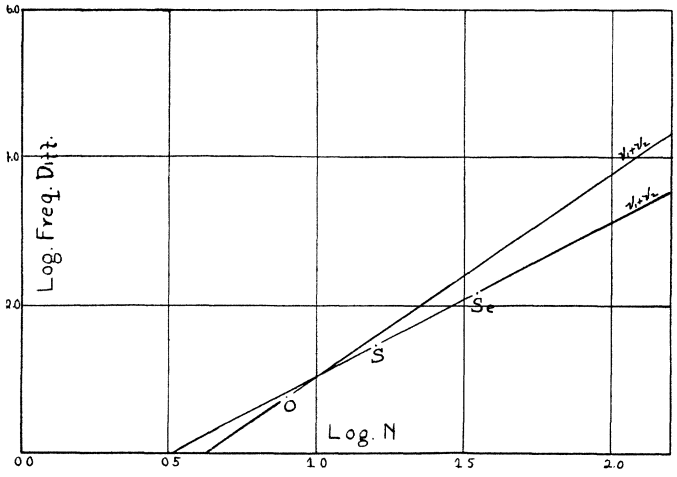

Fig. 5.

ν_1 and ν_2 should be given by parallel equations with $B = 8 \times .479$, and

$$B = \left[\left\{\left(\frac{1}{7}\right)^{2.160} - \left(\frac{1}{8}\right)^{2.160}\right\}\left(\frac{1}{.479}\right)^{2.160}\right]^{-1/2.160}.$$

These values give

$$\nu_1 + \nu_2 = 21.12 + 7.27 = 28.39 \text{ for S,}$$

and $111.63 + 37.04 = 148.67$ for Se. Better agreement would have been obtained if the values for B predicted for Li, K, Rb and Cs had been used.

The analogy suggests that the triplets in O may be given by the equations derived from the triplets in copper. Using these equations we obtain $\nu_1 + \nu_2 = 5.43$; $\nu_1 = 3.80$; and $\nu_2 = 1.61$. The observed differences as given by Runge and Paschen[1] are $3.70 + 2.08 = 5.78$.

The only other group where series of the first type have been worked out, with the exception of those in manganese, is in the third, where

[1] Runge and Paschen, Annalen der Physik, LXI., p. 641, 1897; Astrophysical Journal, VIII., p. 70, 1898.

doublets occur. The graph is shown in Fig. 6. The values of the constants derived from the frequency differences which are known are shown in Table IV.

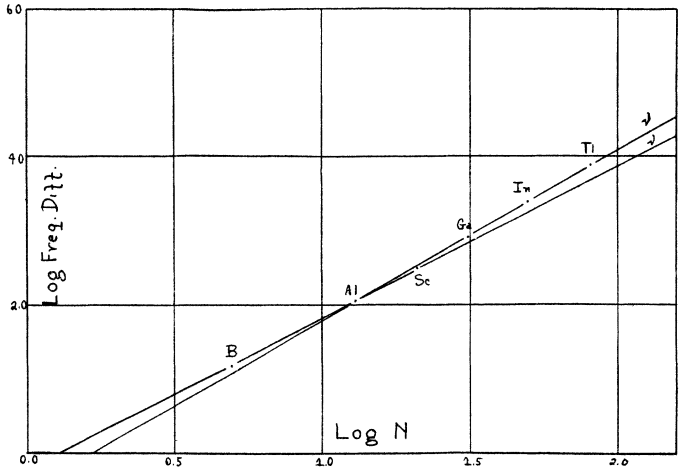

Fig. 6.

TABLE IV.

Element.	*N.*	ν Obs.	ν Calc.	ν Calc. − ν Obs.
Al	13	112.07	110.9	− 1.2
Ga	31	823.6	829.5	+ 5.9
In	49	2212.63	2397.1	+184.5
Tl	81	7792.45	7753.5	− 39.0
B	5	15.4	12.09	− 3.4

$A = 2.318$
$B = 1.706 = 7 \times .246$

It is seen that the value of the doublet separation in boron lies above the line connecting the points determined by the other elements which are alternate members in the family. If another line should determine the frequency differences for the other elements B should lie on it, and it should intersect the known line in the neighborhood of the point determined by Al. Hicks[1] has found a doublet difference for scandium of 320. Combining this value with that known for boron we find that $A = 2.166$, and $B = 1.433 = 6 \times .239$.

DISCUSSION.

The results stated show that the logarithmic method of obtaining the relation between atomic number and frequency differences in spectral

[1] Hicks, Philosophical Transactions, A, CCXIII., p. 408.

series give comparatively good agreement between the observed and calculated values for the constant frequency differences for elements of low atomic number, although the agreement is not within the limit of probable error of the mean of the observed differences, the probable error of the observed value being usually not more than 0.5 cm^{-1}. For elements of high atomic weight the observed values are greater than the calculated, as should be expected if the mass of the electron varies with its velocity. The logarithmic line should, therefore, curve upwards for elements of high atomic weight. Attention is also called to the fact that the calculated values are all too high for the elements which just precede the rare earths in the chemical table.

The importance of the logarithmic line does not lie so much in an attempt to obtain good agreement between observed and calculated values as in the connections which are brought out between different types of series in the same and different chemical families. The equations derived show that the values of B are successive integral multiples of the same constant for the ν, $\nu_1 + \nu_2$, and ν_1 lines in an element. This seems to mean that the frequency differences between the longer wave-length line in triplets and each of the other two are more important than the differences between adjacent lines. The equations give the same value for A[1] for all separations in the same system, and the constants B seem to be integral multiples of the same constant, 0.080, in all systems. The variation of the value of A seems to indicate that spectral series are of several types, just as there are several types of X-ray spectra. In general, the types vary with the valency of the element, but it is possible for the same type to occur in elements with different valencies as is done in groups I. and VI.

The form of the equation derived does not seem to be predicted from the equation for the frequency of lines as developed by Sommerfeld[2] for X-rays, from which we should expect an equation of the type of Bell's to be approximately true. Sommerfeld's equation, moreover, indicates that the convergence frequency of a series should be given by

$$n_0 = \left(\frac{N-k}{p}\right)^2\left[1 + \frac{a}{4}\left(\frac{N-k}{p}\right)^2 + \frac{a}{8}\left(\frac{N-k}{p}\right)^4 \cdots,\right]$$

where a, k and p are constants, a being a small quantity. Therefore, the convergence frequencies of series of the same type should be approxi-

[1] An inspection of the values for A shows common differences of approximately 0.15, the value 2.60 being the only absent member in such an arithmetic series. It is a curious coincidence that the frequency differences between the α and β lines in the K system of X-ray series may be predicted by the equation $\nu = (N/.065)^{2.58}$.

[2] Sommerfeld, Annalen der Physik, LI., 1916.

mately proportional to $(N - N_0)$.[2] That this is not the case is seen from an inspection of Fig. 7, where the convergence frequencies of the series with constant frequency differences have been plotted. The values used were obtained from Dunz, and may also be found in Kayser's Handbuch der Spectroscopie, Vol. II. The graph shows that an approximate linear relation exists between the convergence frequencies and

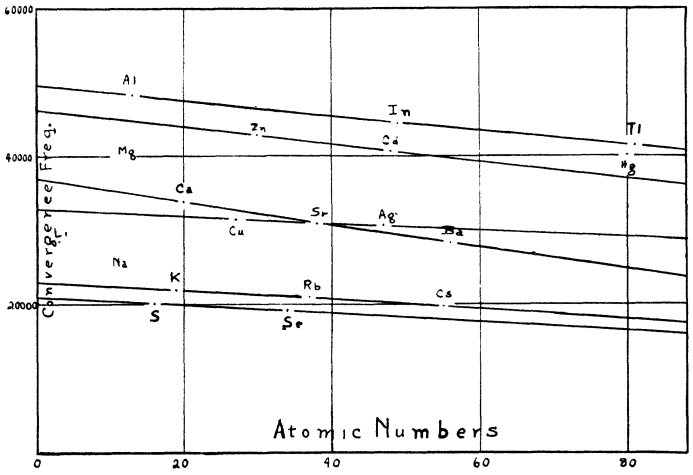

Fig. 7.

atomic numbers of K, Rb and Cs; Ca, Sr and Ba; and Al, In and Tl, which elements I have shown to be related in spectral type. Moreover, a line through the points for S and Se is approximately parallel to that through K, Rb and Cs, a fact which is in support of the hypothesis that the series in these elements is predicted by the same equation.

It would seem that an adequate atomic theory should explain the relation just stated between atomic number and convergence frequency, and the physical reason for the approximate relation

$$\nu = \left(\frac{N}{mnk}\right)^A,$$

where ν represents the frequency difference, N the atomic number, A is a constant, n an integer, both of which vary with the system, m successive integers for the ν, $\nu_1 + \nu_2$, and ν_1 members of the system, and k a constant for all the systems considered.

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