A Critical Study of Spectral Series. Part II: The p and s Sequences and the Atomic Volume Term

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II. *A Critical Study of Spectral Series.—Part II. The p and s Sequences and the Atomic Volume Term.*

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Notation and Abbreviations.

Part I. refers to the First Communication on this Subject in the 'Phil. Trans.,' A, vol. 210, *p.* 57 (1910).

$n = 10^8/\lambda$ = wave number = number of waves per cm.

Adopted formula $n = A - N/(m+\mu+\alpha/m)^2$.

A is the limit of the series = n when $m = \infty$.

ν_1, ν_2 denote the first and second triplet separations.

Δ_1, Δ_2 denote the differences in μ which give rise to ν_1, ν_2.

w denotes the (atomic weight)/100.

v denotes the atomic volume.

Rydberg's notation for the series is adopted. Thus—

P denotes a principal series, S sharp, D diffuse, F the series in the ultra red whose limits depend on the first D sequence. K. and R. call the S the 2nd associated and D the 1st associated series. F is often referred to as Bergmann's series.

ZnS denotes the three sharp series of Zn.

ZnS_2 the second S series of Zn.

ZnS_1 (3) the 3rd line in the first S series of Zn.

HgD_{21} (3), HgD_{22} (3) denote respectively the chief line and the first satellite of the 3rd order in the second diffuse series of mercury.

$N/(m+\mu+\alpha/m)^2$ in any series, say P, is referred to as VP (m), the V standing for variable part.

K.R. stands for Kayser and Runge.

E.H. stands for Exner and Haschek.

The present communication is in continuation of one presented to the Society in 1909. The greater part of the work was completed at that time, and it was hoped that it would be published shortly afterwards. Certain points, however, arose which the author was anxious to settle, and this led to a consideration of a number of spectra in which series of the ordinary type had not yet been recognised. He hopes to deal with some of the most interesting points which have come to light in the

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course of that consideration, chiefly connected with the atomic weight term, and the constitution of certain spectra, in an ensuing paper. In the present one the constitutions of the sequences on which the Principal and Sharp series depend, and their relation to the atomic volume of the element, which were brought to light in Part I., are further considered in connection with the spectra of the second and third groups of elements. It was hoped to have included in the third group the high melting-point sub-group Sc, Y, La, Yb, and considerable progress had been made in reducing their spectra. They all show doublet series of S and D types, but their complete consideration would have taken so much time, better devoted to the general constitutional points which had arisen, that it was decided to postpone it. The evident importance, however, of the comparative study of all the elements in the same group of the periodic system made it seem desirable to give some attention to those elements which might possibly fill the gaps. It is generally acknowledged that these belong probably to elements associated with the rare earths, and their atomic weights give some indication of the places they should fill. Their spectra consist of a multitude of lines chiefly of medium or small intensity, and their complete discussion involves a great deal of time and close attention. All those, however, which the author has so far investigated show more or less analogous relationships, intimately connected, and irresistibly suggesting the *débris*, so to say, of strong lines. The connection is based on certain properties of the atomic weight term referred to above. The evidence of the spectrum of Eu leaves little doubt but that it fills the vacant space between Cd and Hg. Probably the gap between In and Tl is occupied by Gd. A superficial consideration of the spectrum of the latter shows a large number of doublets with a separation of 5000.* This number agrees with its atomic weight and its position between In (2212) and Tl (7792). As is well known, the spectrum of Ra is quite analogous to those of the Ca group, whilst possibly the gap between it and Ba may be filled by another radio-active substance. An attempt has been made to allot the S and D series of Eu and Ra and the result is given in Appendix I. In response to suggestions made to me in respect of Part I., I have ventured to give in a second appendix lists of the S and P series lines of the elements considered in the present communication.

The type of formula used here and in Part I. has been employed by MOGENDORFF in a still earlier paper read before the Royal Society of Amsterdam in November, 1906. He there showed that the formula reproduces the lines of Li, Na, Zn, and Tl in the different series with great exactness, and stated that he had also obtained corresponding formulæ for other elements.

The fact that the series depends in some way on the atomic volume of the element has been pointed out by REINGANUM.† He showed that if the atomic volumes of the 2nd group of elements be divided by 4, and those of the 3rd by 6, and if the

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* There are 53 within ·50 of 5000, or 76 within 1 A.U. of that value.

† 'Phys. Zeitsch.,' 5, p. 302.

logarithms of these modified atomic volumes and of the limits of the S series be plotted, then, with the exception of Zn and In, the corresponding points lie roughly on a straight line.

The p-sequence.—In determining the formulæ constants for the Sharp series, it immediately becomes evident that they are based on the P-sequence, viz., that which in the alkalies give the Principal series. It is impossible to get constants based on the S-sequence to reproduce the lines within considerable multiples of the possible errors. Not only does the P-sequence do so, but it will be found in correspondence that the Principal series are formed on the S-sequence, viz., that which in the alkalies gives the Sharp series. Confirmatory evidence is also afforded from the facts that the relationships between the constants are of a similar kind to those found in the alkalies and that the limit of the Principal series (S-sequence) is the same as the variable part of the first line of the Sharp whilst that of the Sharp is not rigorously the same as the variable part of the first line of the Principal. In other words, VP and VS denoting sequences, the limit of the Principal series is VP (1), whilst that for the Sharp series deviates considerably from VS (1). This fact renders the notation of the sequences introduced in Part I. confusing. The confusion may, however, to some extent be avoided if small letters are used to denote sequences and large letters the lines or series. Thus, in these elements VP $(m) = s\,(m)$ and VS $(m) = p\,(m)$.

The features of the p-sequence, as developed in Part I., are (1) $\mu = 1+f$ where f is a fraction (2) if the denominator be written in the form $1-\mathrm{W}\,(1-m^{-1})+\mu+\alpha m^{-1}$, where W is the atomic weight term, α is negative, α/μ is a constant (·215), μ is proportional to the atomic volume of the element, and $p\,(1) = \mathrm{S}\,(\infty)$. The s-sequence has (1) $\mu = f$, α negative, μ about ·5 less than the corresponding value for the principal and $s\,(1)$ is not $\mathrm{P}\,(\infty)$ but very nearly so, being always slightly less.

In the alkalies it was found necessary, if RYDBERG's relations between the limits of the S and P series were to be valid, that a very small term in m^{-2} had to be applied, although it was unnecessary, so far as reproducing the lines within observational error was concerned. In the present case, also, no term in m^{-2} is required for the Zn or Tl groups. In the alkaline earths themselves such a term βm^{-2} is required, β, however, being a small fraction of α.

The formulæ constants determined for the various elements are given in Table I. They are determined, as a rule, by taking the measures of the first three lines as having no observational errors, the limits of variation of constants due to these possible observational errors being given in brackets, as in Part I. It is found, however, that in the case of Zn, Cd, Hg, Sr it is necessary to allow for these errors if the subsequent lines are to come within observational limits. In these cases the constants have been slightly modified within permissible limits so as to bring all within, and the numbers attached to the constants in the tables are limits allowable on these modified constants. There is some uncertainty in the case of Ba. The series is ill defined. No lines were assigned by KAYSER and RUNGE to the S series—

TABLE I.

	S (∞).	μ.	α.	β.	ν, Δ.
Mg . . .	39752·83 (2·73) 39758·38 (1·12)	1·382492 (3605) 1·376746 (419)	− ·075952 (9336) − ·062211 (257)	·008307 (5890)	40·92, 19·87 ·000856, ·000413
Ca . . .	33983·45 (5·80) 33994·85 (1·10)	1·574562 (7058) 1·561400 (498)	− ·108386 (17663) − ·077202 (438)	·018813 (10986)	105·89, 52·09 ·002791, ·001368
Sr . . .	31027·65 (4·00) 31037·27	1·643036 (5868) 1·631491	− ·111113 (14501) − ·083879	·016412 (8969)	394·38, 186·95 ·011836, ·005533
Ba . . .	28642·63	1·672500	− ·054144		878·21, 370·33 ·029328, ·011976
Ra . . .	22760·00	1·783424	− ·176286		2050·26, ? ·092658, ?
Zn . . .	42876·42 $\begin{pmatrix}+3·34\\-1·08\end{pmatrix}$	1·287059 $\begin{pmatrix}-1059\\+\ 461\end{pmatrix}$	− ·059160 $\begin{pmatrix}-1059\\+563\end{pmatrix}$		389·20, 190·21 ·007207, ·003475
Cd . . .	40710·60 $\begin{pmatrix}+2·15\\-\ \ ·73\end{pmatrix}$	1·349486 $\begin{pmatrix}-846\\+294\end{pmatrix}$	− ·067133 $\begin{pmatrix}-738\\+264\end{pmatrix}$		1170·85, 542·02 ·023106, ·010370
Eu . . .	40364·08 40397·87	1·291603 1·267384	− ·047520 − ·010971		2630, 1004 ·051222, ·018327
Hg . . .	40139·55 $\begin{pmatrix}+5·41\\-\ \ ·99\end{pmatrix}$	1·309577 $\begin{pmatrix}-1700\\+300\end{pmatrix}$	− ·068280 $\begin{pmatrix}-1438\\+\ 272\end{pmatrix}$		4630·46, 1767·01 ·087815, ·030002
Al . . .	48161·46 (2·49)	1·250525 (771)	− ·063349 (662)		112·15 ·001754
Ga . . .	46318·16 (?)	1·292185	− ·077314		826·10 ·013542
In . . .	44454·76 (2·48)	1·287479 (870)	− ·069510 (769)		2212·38 ·037684
Gd . . .	?				5000
Tl . . .	41470·23 (1·72)	1·264328 (534)	− ·070417 (456)		7792·39 ·134153

In the above table the two values given for Mg, Ca, Sr correspond respectively to the cases with βm^{-2}, and without the term in β. The last column gives in the first line the values of the doublet or triplet separations (ν_1 and ν_2), and in the second line the values of the Δ, *i.e.*, the quantities deducted in the denominator of $S_1(\infty)$ to give $S_2(\infty)$; in other words, they are the atomic weight terms on which ν_1, ν_2 directly depend.

in fact, they only observed the triplet S (2), S_1 (3), S_2 (3) of the next and S_1 (4)—too few to give the series. The triplet S (1) was observed first by LEHMANN* (more accurately later by HERMANN†) and the series completed and arranged by SAUNDERS.‡ The first three are only sufficient to determine the constants with α only; in the analogous cases of Mg, Ca, and Sr the limits so determined have all come out too large. Here it makes the calculated values of wave numbers for S_1 (4) and S_1 (5) differ from those assigned by SAUNDERS by amounts too large respectively by 71 and 159—in other words, the limits here, also, are much too large if his allocations are correct. If we use his allocation of S_1 (4) and attempt to find constants for βm^{-2} we get a formula quite out of line with the others. The first impression is to infer that SAUNDERS' allocation of the two last lines is quite wrong, but a closer acquaintance with other series gives more caution and suggests another way of meeting the difficulty. As a fact, it is difficult to represent all the P series, and especially the D series by any modification of the simple formulæ hitherto used. In the case of AlD it seems impossible to do so at all. Further, it will be shown in Part III. that the atomic weight term plays a very important part in producing new lines or displacing expected ones.

New lines are produced by the addition (or subtraction) of multiples of the atomic weight term to the denominators in the formulæ which irresistibly suggest modified molecular groupings. The full evidence for this can only come later when these lines are being discussed, but as bearing more especially on this part of the subject it will be convenient here to show how it enables us to explain why in the alkalies RYDBERG'S relations $S(\infty) = p(1)$ hold while the other $P(\infty) = s(1)$ does not. (F, G of Part I., pp. 75–76.)

If the first term of a series is modified by the addition of a number to the denominator, it may still be possible to represent the series by a formula containing αm^{-1} only. If, however, the second be also changed in a similar way, it will in general not be possible to do so. We shall require a third term, βm^{-2}, so that the successive changes in the denominator produced by the two alterations may be represented. If a change be also made in the third line, it may still be possible to retain βm^{-2} only because it is an addition to a large number (m large), and it may still be possible so to apportion the four formulæ constants that the calculated results err by amounts less than the observational errors. In general, however, the limit will be considerably wrong. In Ca and Sr the limit with βm^{-2} is certainly very nearly the correct value. But, as above mentioned, βm^{-2} is not sufficient for Ba. Now we have before us the results of the discussion of the alkalies, where it was found that if RYDBERG'S relations (*i.e.*, F, G) are both to hold the p-sequence must have a small term βm^{-2} and the s-sequence a term βm^{-2}, in which β is of the same

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* 'Ann. der Phys.' (4), 8, p. 650 (1902).

† 'Ann. der Phys.' (4), 16, p. 698 (1905).

‡ 'Astro. Phys. Jour.,' 28, p. 223.

order as the α. But the difficulty may be met as follows: If D denotes the denominator of $s(1)$ and D′ that of $P(\infty)$, the values of D−D′ instead of being zero are respectively (see Part I., p. 76)—

Na . . . ·002772±(8390); Rb . . . ·010696+(16119), −(3210);
K . . . ·009150±(8716); Cs . . . ·01672± ?

The values of 2W or Δ are given at the bottom of p. 80, viz.:

Na.	K.	Rb.	Cs.
·000744,	·002933,	·012887,	·032435,

whence*

$$\begin{aligned} 8W &= \cdot 002976 = \cdot 002772 + 1/41 \times \text{possible error for Na,} \\ 6W &= \cdot 008799 = \cdot 009151 - 1/25 \times \quad ,, \quad ,, \quad \text{K,} \\ 2W &= \cdot 012887 = \cdot 010696 + 1/8 \times \quad ,, \quad ,, \quad \text{Rb,} \\ W &= \cdot 016217 = \cdot 016712 - \ ? \quad ,, \quad ,, \quad \text{Cs.} \end{aligned}$$

It is thus possible to assert the truth of RYDBERG's relations if they are referred to the sequences—but not if referred to the series. The value of the first line of the S series is found by adding a multiple of the atomic weight term to the sequence term for that line, viz., 8W for Na, 6W for K, 2W for Rb, and W for Cs. The essential point now is that the term in βm^{-2} does not enter. In any case the multiple is to be obtained by first determining the real limit of the series and then the change in the denominator calculated for $m = 1$ to correct it to the observed value. This suggests a similar explanation for the appearance of the βm^{-2} terms in the Ca group, either an addition of an atomic multiple to the first term of the p-sequence, or the deduction of the same multiple from every term after the first, and this suspicion is intensified when we notice that the values of the β are themselves multiples of the atomic weight terms. If we compare the values of β and of Δ_2, given in Table I., this is at once clear. We find with extreme closeness

Mg.	Ca.	Sr.
$\beta = 20\Delta_2$,	$14\Delta_2$,	$3\Delta_2$.

To obtain the proper values for the limit it is found necessary to deduct from the observed denominators respectively $5\Delta_2$, $5\Delta_2$, Δ_2. Ba is too uncertain to get definite results from. If all SAUNDERS' lines belong to BaS and the modification depends on an addition to the first term only, it is necessary to deduct $12\Delta_2$ from the first and the μ and α become so large in comparison with the values for the other elements as to render the explanation very doubtful. It can, of course, be met by deducting multiples from the second line as well as the first, but we can have no certain grounds

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* Too much weight must not be given to these as the possible errors are so large.

to work upon until we can get some evidence as to what the limit really is. The constants determined for the three elements in this way are given in the following scheme. Values for Ba are also given on the supposition that Δ_2 is subtracted in the same way as for Sr.

For

Mg . .	$n = 39754{\cdot}31 - \mathrm{N}/\{m + 1{\cdot}379975 - {\cdot}067249m^{-1}\}^2$	add $5\Delta_2$	for $m = 1$,
Ca . .	$n = 33981{\cdot}96 - \mathrm{N}/\{m + 1{\cdot}572477 - {\cdot}094220m^{-1}\}^2$	,, $5\Delta_2$	,,
Sr . .	$n = 31027{\cdot}58 - \mathrm{N}/\{m + 1{\cdot}640373 - {\cdot}097552m^{-1}\}^2$	,, Δ_2	,,
Ba . .	$n = 28619{\cdot}23 - \mathrm{N}/\{m + 1{\cdot}692912 - {\cdot}084616m^{-1}\}^2$	,, Δ_2	,,

In the following Table II. a comparison of the calculated values with the observed is given. The first column under the element gives the maximum permissible error and the second the difference between calculated and observed. The third column, under Mg, Ca, Sr, gives the same difference when the lines are calculated from the formula in βm^{-2}. Under Eu no estimates of observational errors are available, and the two columns refer to the two series referred to in the text below and in Appendix I. In all cases the deviations are only given for the first lines of a doublet or triplet.

It will be seen that the only real deviations from observed values greater than the possible are for TlS (4) and CaS (5). In the case of TlS (4) the doublet separations given by the observed values is too small by 1·5, and the calculated value corrects this. The whole of the calculated values agree so closely with the observed as to make it certain that the error must be in the observed. The observed is 2665·67—a transcription error of 2665·76 would bring the two sets in agreement. As to the case of CaS (5) the line 3181·40 also gives an incorrect separation ν_1 which the calculated corrects. It has an observed accuracy of ·03 A.U., and the calculated differs by 15 times this amount. It should be noticed, however, that its intensity is higher than we should expect, viz., 4 as against 1 for S (5). Moreover it is an enhanced line and therefore does not belong to the S-series. It is probable, therefore, that it hides the true S line, which should be about 3181·00 and of less intensity.

A curious point is that in In the S_2 lines appear to be more persistent than the S_1. KAYSER and RUNGE give a line 2200·0 as $S_2(8)$, with possible error ·30. The calculated, however, deviates by more than 5 times this from the observed, and as the formula reproduces the other lines with good accuracy it is probable that 2200 is wrongly assigned to S, or should be 2201·6.

Connection of α and μ.—The study of the alkalies led to the result that the denominator of the p-sequence can be thrown into the form $m + 1 - \mathrm{W}(1 - m^{-1}) + a(1 - km^{-1})$, where W is the atomic weight term, and k is a constant which is about ·21520, the only exception was for Cs for which a slight modification was required. It is important to see whether a similar relationship holds for the analogous sequences in the elements now under consideration. In the alkalies W is one-half the difference

TABLE II.

	Mg.			Ca.			Sr.			Ba.		Zn.		Cd.		Eu.			Hg.		Al.		Ga.		In.		Tl.	
m.	O.	m^{-1}.	m^{-2}.	O.	m^{-1}.	m^{-2}.	O.	m^{-1}.	m^{-2}.	O.	m^{-1}.	O.	m^{-1}.	O.	m^{-1}.	O.	I.	II.	O.	m^{-1}.	O.	m^{-1}.	O.	m^{-1}.	O.	m^{-1}.	O.	m^{-1}.
1	·03	·00	·00	·1	·00	·00	·12	·00	·00	?	·00	·03	·00	·05	·00		·00	·00	·05	·00	·03	·00	·10	·00	·10	·00	·03	·00
2	·03	+ ·02	·00	·05	·00	·00	·03	·00	·00	·05	·00	·03	·00	·05	− ·02		·00	·00	·05	·03	·03	·00	·05	·00	·05	·00	·03	·00
3	·03	− ·02	·00	·05	·00	·00		·00	·00	·05	·00	·05	− ·04	·03	·01		·00	·00	·10	− ·07	·05	·00	·05	·00	·05	·00	·05	·00
4	·03	·07	·02	·10	·33	·00	·10	·23	− ·05			·10	·01	·05	·02		·14	− ·01	·05	·03	·10	− ·02			·05	·04	·05	−1·21
5	·15	·15	·01	·03	1·15	·61	·30	·69	+ ·09			·15	·01	·10	·00		− ·36	− ·02		·02	·10	− ·02			·15	·13	·05	− ·02
6	·50	·10	− ·01	1·0	·46	− ·23						·25	− ·15	·30			?	− ·34		·00					·50	− ·12	·10	·00
7																	−1·12	+ ·20		− ·01					·30	·03	·15	·02
8																		− ·54		·04					?	1·8	·20	·12
9																				− ·03						·35	·20	− ·18
10																				·07							·30	− ·02
11																											·30	·03
12																				− ·10							·30	·12
13																				·19							·30	− ·19
14																												

(Δ) of the denominators which give the doublet separations. Here, however, triplets enter and two constants Δ_1 and Δ_2 appear. It is found that the Zn, Cd, Hg group follows the same rule if W is taken to be Δ_2, which is roughly one-half of Δ_1, but, as in the case of Cs, a modification is required for the high separations of Hg. Using the numbers given in Table I., it will be found that the following forms for the denominators hold:—

$$\begin{array}{lll}
\text{Zn} \;.\;\;.\;\;. & m+1-\text{W}\,(1-m^{-1})+{\cdot}290534\,(1-{\cdot}21558m^{-1}), & \begin{array}{l}-(762)\\+(606)\end{array}\\
\text{Cd} \;.\;\;.\;\;. & m+1-\text{W}\,(1-m^{-1})+{\cdot}359854\,(1-{\cdot}21537m^{-1}), & \begin{array}{l}+\;\;(55)\\-(160)\end{array}\\
\text{Eu} \;.\;\;.\;\;. & m+1-\text{W}\,(1-m^{-1})+{\cdot}309930\,(1-{\cdot}21246m^{-1}),^{*} & \\
\text{Hg} \;.\;\;.\;\;. & m+1-\text{W}/4 \qquad\qquad\quad +{\cdot}317077\,(1-{\cdot}21534m^{-1}). &
\end{array}$$

The numbers in brackets after each formula give respectively the possible limits of variation of the k. It is clear that, as in the alkalies, k can easily be the same for all.

In Mg and the Ca sub-group we have the complication of the additional terms in βm^{-2}, or of the modified form of the sequence itself with αm^{-1} only. In the first case β, as we have seen, is a multiple of Δ_2. The constant ratio k does not enter now unless we use β in place of Δ_2, in which case there results

$$\begin{array}{lll}
\text{Mg} \;.\;\;.\;\;. & m+1-\;\;\beta\,(1-m^{-1})+{\cdot}382462\,(1-{\cdot}21533m^{-1})+\beta m^{-2}. & \beta = 20\Delta_2,\\
\text{Ca} \;.\;\;.\;\;. & m+1-\;\;\beta\,(1-m^{-1})+{\cdot}574797\,(1-{\cdot}21572m^{-1})+\beta m^{-2}. & \beta = 14\Delta_2,\\
\text{S} \;\;.\;\;.\;\;. & m+1-2\beta\,(1-m^{-1})+{\cdot}676156\,(1-{\cdot}21404m^{-1})+\beta m^{-2}. & \beta = \;\;3\Delta_2,\\
\text{Ba} \;.\;\;.\;\;. & \quad ? &
\end{array}$$

The modified form does not so naturally fall into line. It is, of course, only a matter of calculation to put in a term $x\,(1-m^{-1})$ such that the ratio of α/μ left over is the same constant as in the other cases. If we confine ourselves to multiples of Δ_2 or of $\Delta = \Delta_1+\Delta_2 = 3\Delta_2$ roughly, and use multiples of these to give α/μ as nearly as possible constant, we get the following results:—

$$\begin{array}{ll}
\text{Mg} \;.\;\;.\;\;. & m+1-15\Delta\;\,(1-m^{-1})+{\cdot}399010\,(1-{\cdot}21624m^{-1}),\\
 & m+1-45\Delta_2\,(1-m^{-1})+{\cdot}398605\,(1-{\cdot}21545m^{-1}),\\
\text{Ca} \;.\;\;.\;\;. & m+1-\;\;9\Delta\;\,(1-m^{-1})+{\cdot}609908\,(1-{\cdot}21585m^{-1}),\\
 & m+1-27\Delta_2\,(1-m^{-1})+{\cdot}609413\,(1-{\cdot}21522m^{-1}),\\
\text{Sr} \;.\;\;.\;\;. & m+1-\;\;3\Delta\;\,(1-m^{-1})+{\cdot}692393\,(1-{\cdot}21602m^{-1}),\\
 & m+1-\;\;9\Delta_2\,(1-m^{-1})+{\cdot}690053\,(1-{\cdot}21336m^{-1}),\\
\text{Ba} \;.\;\;.\;\;. & m+1-\;\;2\Delta\;\,(1-m^{-1})+{\cdot}775746\,(1-{\cdot}21584m^{-1}),\\
 & m+1-\;\;7\Delta_2\,(1-m^{-1})+{\cdot}776744\,(1-{\cdot}21685m^{-1}).
\end{array}$$

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[*] Might quite possibly be ·215, see Appendix I. [also note at end].

These last arrangements are, of course, no argument in favour of the constant ratio ·21520. They can only be regarded as suggestions of the way in which the $1-m^{-1}$ term may enter if we know that the constant ratio has a real existence, and that this modified sequence is the correct form. But in the present state of our knowledge nothing is to be gained by attempting a closer approximation. It may, however, be noted that the general agreement between the two arrangements Δ and Δ_2 is due to the fact that except for Ba Δ is roughly $3\Delta_2$. Also as affecting the argument in favour of the arrangement, it may be mentioned that a change of unity in the multiples of Δ or Δ_2 in the most favourable direction towards the value ·21520 affects that ratio in the two cases as follows, viz.:—

For Mg . . ·21380, ·21626; Ca . . ·21054, ·21697; Sr . . ·19588, ·21960;

and, of course, very much larger deviations for Ba.

A glance at Table I. shows that in Al and the Ga sub-group the α is always larger than $\cdot 215\mu$. In fact, the actual ratios of α/μ are

Al . . ·2528; Ga . . ·2641; In . . ·2419; Tl . . ·2664.

These cannot be the same within observation limits, and even in the Ga sub-group In is too far out to be due to mere errors of observation. It is clear, therefore, that no terms in $1-m^{-1}$ can occur in the same way as in the other cases.

In the discussion of the alkalies the term $W(1-m^{-1})$ was supposed to be based on the F-sequence, which was taken to be $m+1-2W(1-m^{-1})$. Here we have only two lines each in Al and Tl allocated to the F* series by RITZ, whilst those for the other elements of this group have not yet been observed. The limits of the F series are the values of VD (2). Using this, the denominators of the F series are found to be

$$\text{Al} = m+1-\cdot 043761\,(1-m^{-1}),$$

$$[25\Delta = 50\text{W} = \cdot 043850 \pm (24)],$$

$$\text{Tl} = m+1-\cdot 037389\,(1-m^{-1}).$$

If now as before the p-sequence be supposed based on the F-sequence, but that the factor $1-m^{-1}$ does not now occur, the denominator for Al may be written

$$m+1-\cdot 043761+\cdot 294286\,(1-\cdot 21526m^{-1}).$$

Unfortunately we are not able to compare with the other elements of the Al sub-group (Sc, Y, La) to see if they follow an analogous rule; but the appearance of the

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* Called by some German writers BERGMANN'S series, as he discovered the analogous series in the alkalies.

constant ratio is at least suggestive. A similar arrangement does not hold for Tl, but we have been led not to expect it in the highest atomic weight of a group. If we define W as before, viz., $2W = \Delta$, we can write for the formulæ

$$\begin{aligned} \mathrm{Al} &= m+1-50W+\cdot 294286\,(1-\cdot 21526m^{-1}), \\ \mathrm{Ga} &= m+1-10W+\cdot 359895\,(1-\cdot 21483m^{-1}), \\ \mathrm{In} &= m+1-\ \ 2W+\cdot 325202\,(1-\cdot 21478m^{-1}), \\ \mathrm{Tl} &= m+1-\ \ \ \ W+\cdot 331405\,(1-\cdot 21248m^{-1}). \end{aligned}$$

Ga and In may give ·21520 within observation limits.

The foregoing results, combined with those previously obtained for the alkalies, produce a strong conviction that the number ·21520 is an essential constant—possibly for all elements—but at the same time raise the question of the cause why they do not follow precisely the forms shown by the alkalies, the Zn group, and to some extent by the alkaline earths.

Atomic Volume Term.—In the spectra of the alkalies it was found that when the p-sequence was thrown into the form considered above the μ was very nearly proportional to the atomic volume, and still more nearly so if the denominators were written $m+\cdot 987\ldots+$, &c. Since the atomic weight term disappears when $m = 1$ the same result should hold for the denominator of $p(1)$, with the advantage that this can be determined much more precisely than μ. The value of the atomic volume of an element as calculated from its atomic weight and density must have some degree of indefiniteness, depending as it does on the temperature and physical state of the substance when its density is measured. Nevertheless there must be some physical property peculiar to each element of which the atomic volume as usually determined is a rough measure, and it is this which would occur in the spectral formulæ if the relation indicated in the alkalies is a reality. Probably the relation between this physical constant and the atomic volume would be exact if the latter were determined at absolute zero. Failing the possibility of doing this we might try to extrapolate downwards by using the coefficient of expansion determined at ordinary temperatures, or compare the substances in corresponding states, say at the melting-points. In this first survey, however, it is needless to attempt such refinement, and we shall confine ourselves to seeing what evidence there is that such relationships do enter, and try to get a rough idea of the way in which they do.

It will be better to discuss the relationship on the basis of the denominator of $p(1)$ rather than μ, the former being less dependent on errors of observation. In Part I. the quantities in question were considered as being proportional to the atomic volume, but as a result of the discussion below it will be found best to consider them as proportional to twice the atomic volume. The constant of the ratio for the alkalies was not determined; but the values of the denominators there given, combined with the values of the atomic volumes given by RICHARDS and BRINK,* lead to values of D/2v, given by the first line of figures in the following table:—

Na.	K.	Rb.	Cs.
·002466 ·002761	·002578 ·002732	·002615 ·002740	·002541 ·002640

the values for Cs being very uncertain. The values show first a gradual rise with atomic weight, and then a fall. The fall of melting-point, *i.e.*, increase of the measured atomic volume on nearing the melting-point, would explain a fall in the ratio shown by Cs. The first rise must be explained by another cause. Now, it was pointed out in Part I. that the proportionality (α/μ) was closer if the denominators were measured from about ·986 instead of 1, the number ·986 having appeared in quite another relation. In other words, a number about ·014 should be added to the fractional part of the denominator. If this be done, the results obtained are shown in the second line of figures in the above table. In this case, the exactness of the ratio is striking, the fall in Cs being probably due to error of formula as well as closeness of melting-point. We may take the ratios as very close to ·002740. This is for the alkali elements. It now remains to see whether any similar relationships hold for the elements here considered.

Taking first the Zn sub-group, the following values are obtained from Table I. for the values of the fractional parts of the denominators of $p(1)$, *i.e.*, of VS (1):—

Zn . . ·227900; Cd . . ·282353; Eu . . ·244083; Hg . . ·241297.

The densities at ordinary temperature, as given in LANDOLT and BÖRNSTEIN, are respectively

Zn . . 7·01; Cd . . 8·65; Eu . . ? ; Hg . . 13·55;

which give for the atomic volumes at ordinary temperatures

9·33, 13·00, ?, 14·76.

It is clear, at a glance, that the above denominators cannot be proportional to the atomic volumes, but it is easy to show that in Zn, Cd, and Hg they are respectively proportional to 9v, 8v, and 6v. In fact, the ratios to these come out to

$$·002715 \times 9v, \qquad ·002715 \times 8v, \qquad ·002725 \times 6v.$$

The ratios show a remarkable agreement with themselves and also with those of the alkalies when referred to ·986. The practically exact equality of the above

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* 'Jour. Amer. Chem. Soc.,' 1907, p. 117.

numbers must be due to chance, for they would be altered by the slight alteration in density as measured in different physical conditions. We should be prepared to expect a considerable difference in the number for Hg, as it is so far above its melting-point. Without, however, giving any special weight to the exactness of the agreement, it yet affords strong evidence for the dependence of the *p*-sequence on the real atomic volume in the manner indicated. If Eu behaves in an analogous way we should expect it to be proportional to $7v$, *i.e.*, $\cdot 244083 = \cdot 002720 \times 7v$ or $v = 12\cdot 86$, whence, taking the atomic weight of Eu to be 152·03,* the density of Eu at ordinary temperatures should be about 11·86, *i.e.*, intermediate between those of Cd and Hg, as is to be expected.

In the case of the alkaline earths we have to consider the two forms of the sequence—(1) that involving βm^{-2}, and (2) that in which multiples of Δ_2 are added to give the first spectral line of the series. Also, in the first form the question arises whether the quantity to be discussed should be the denominator of VS (1) or with β left out. In fact, if the atomic volume term is the factor μ when the denominator is thrown into a form containing a term $\mu(1-\cdot 21520 m^{-1})$, then the quantity to be considered would be the latter, assuming the results given in (p. 41). For comparison both cases are treated, 1 (*a*) and 1 (*b*), in the table below. The fourth line gives the numbers for Case (2). As in the Zn sub-group it will be found that multiples of v enter.

	Mg (8*v*).	Ca (7*v*).	Sr (6*v*).	Ba (6*v*).	Ra (*xv*).
Density	1·72	1·57	2·54	3·77	1·02*x*
1 (*a*)	·002783	·002731	·002649	·002862	
1 (*b*)	·002710	·002625	·002570	?	
2	·002764	·002693	·002623	·002782	

The densities used in calculating are the means of those given by Landolt and Börnstein; the values for Ca and Sr are not very accurate. In the case of Sr the density is given as between 2·50 and 2·58; the latter would alter the numbers above for Sr to ·002664 in Case (2) and ·002690 in Case 1 (*a*) The number for Ba is calculated on the doubtful basis of (p. 39), and it is necessary to take a multiple of $6v$. If Saunders' allocation be correct the value of S (∞) is very much less, and the value of the denominator of VS (1) is close to 1·492765. In this case, if a multiple $5v$ is taken, the ratio is ·002705. Moreover, this ratio is in analogy with the others, and, so far, it adds weight to Saunders' allocation. It is quite possible that the value of SrS (∞) is too high, which would result in too small a value for the ratio. The numbers, however, are sufficiently close for all these elements to afford additional

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* Jantsch, 'C. R.,' 1908, vol. 146, p. 473.

evidence for the dependence on atomic volume.* In doing so, however, the best result is obtained by 1 (*a*), *i.e.*, by taking the values of the denominator of VS (1) without any modification, although (2) is nearly as good.

The density found for Ra, using as constant ·002740, is 1·02x, where x is a whole number. If the number for Ba is 6, *i.e.*, the same as for Sr, we might expect that 6 might be a limit and $x = 6$ for Ra. If for Ba the ratio is 5, then x might possibly be 5. If, however, the series runs down in regular order, then allowing for the gap between Ba and Ra, x would be 3, giving a density 3·06, *i.e.*, less than that of Ba. If $x = 5$ or 6, the densities calculated are 5·10 and 6·12; either are in fair order with the other elements of the group.

If the elements in the third group are treated in the same way, using the densities Al = 2·583, Ga = 5·95, In = 7·26,† Tl = 11·85, Al does not fall into step with the others. The results are

$$\begin{aligned} \text{Al} &= \cdot 002744 \times 6\cdot 5v, \\ \text{Ga} &= \cdot 002613 \times 7v, \\ \text{In} &= \cdot 002760 \times 5v, \\ ? &= \quad ? \\ \text{Tl} &= \cdot 002816 \times 4v. \end{aligned}$$

The agreement with the supposed law is very unsatisfactory, and in the case of Al is clear against it. Al is the case where, in order to produce the ·21520 constant, the μ had to be referred to the F-sequence (p. 42), which produced an addition to μ of ·043761. If this be done in this case also, the value of the denominator comes out to be ·002751 × 8v. This is so close to the law that it suggests the possibility of the elements of the third group behaving like the alkalies—themselves elements with doublet series. In that case it was found necessary to refer the quantities in question to ·986 + f, *i.e.*, add ·014 to the $\mu+\alpha$, where ·986 was a constant for the whole group. If so the result for Al would indicate that the constant for the third group should be ·956239, *i.e.*, (1 − ·043761), or that the quantity ·043761 should be added to the $\mu+\alpha$ as found. If this is done the following scheme results:—

Al.	Ga.	In.	Tl.
·002751 × 8v,	·002752 × 8v,	·002758 × 6v,	·002761 × 5v,

which recalls the close agreement found with the Zn group.

Probably the F-sequence depends on the group constant (·956) plus a multiple of the atomic weight term. For Al this is very small, so that the group constant would be somewhat smaller than ·9562 determined from the F. The difference would not appreciably affect the coefficients above. This would explain, however, the apparent

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* These results for the two groups were given in a paper read before Section A of the British Association at the Sheffield meeting (1910). 'Rep.,' p. 574.

† Mean of values given by LANDOLT and BÖRNSTEIN.

dependence of the value required on the F-sequence of Al, whilst the corresponding value from Tl is very different, viz., ·962661. For suppose the F-sequence takes the form $m+$ group constant $+\Delta(1-m^{-1})$ (see Part I.). The Δ for Al and Tl are respectively ·001754 and ·134153, whilst m is always 2 for the first line of the F series. Hence the difference of the values of the denominators of the F series of Al and Tl is $\frac{1}{2}$(·134153−·001754) = ·06620, whilst the values found are ·962611−·956239 = ·006372, sufficiently close to show that the above explanation may be on the right lines. The fact that ·014 and ·0437 are in the ratio 1 : 3, *i.e.*, of the valencies of the Groups I. and III., may be a coincidence, but should be borne in mind for future testing. The results for these two groups suggest a similar kind of group constant for Zn and the Mg sub-groups of II., but if so no F series have yet been observed to determine them. It is at least to the point to notice that such a term would raise the coefficients of the Zn set (·002715) more to an equality with the values (·002755) of the Al set.

The evidence for the dependence of the p-sequence on the atomic volume is therefore strong from all the cases in combination. The actual value of the constant (·002740) cannot be accurately determined as yet, because we have no knowledge of the actual value for any element of the physical quantity we denote by "atomic volume"; but it is probably not far from ·002740. The results of the foregoing discussion therefore point to the p-sequence being of the form $a(1-km^{-1})sv$, where a and k are constants for all elements, not very different from ·002740/$(1-k)$ and ·21520 respectively; v is the essential atomic volume of the element (possibly sphere of activity), and s is a whole number. How s depends on the position of the element in its group is a problem which it is to be hoped further knowledge may solve. Putting k = ·21520 makes a approximately = ·003490.

The values of s for the elements so far considered are as follows:—

Na 2	Mg 8	Zn 9	Al 8	Ga 8
K 2	Ca 7	Cd 8	Sc ?	In 6
Rb 2	Sr 6	Eu 7 ?	Y ?	?
Cs 2	Ba ? 5 or 6	Hg 6	La ?	Tl 5
	?		Yb ?	
	Ra ? 5 or 6			

The Term in W $(1-m^{-1})$.—This term does not affect the first line in the series, and its appearance would seem to indicate the possibility of some modification of the formula. In the course of some calculations connected with the Zn series, it was noticed that the lines could be reproduced when this term was absent provided the value of N was slightly altered for all terms beyond the first. It seemed worth while to test whether a similar connection held for other elements. The method adopted was to use the limit obtained by the earlier formulæ, calculate the denominator in VS (1), throw it into the form $\mu(1-{\cdot}21520m^{-1})$ $(m = 1)$, use this as the denominator for the succeeding terms and calculate the value of N required to reproduce the observed value. These were then corrected so that the separations of the S_1, S_2, and S_3 lines should have the constant value found for ν_1, ν_2. As an example, the case of Zn may be taken. The limit is 42876·42 and $D_m = m+1+{\cdot}290534\,(1-{\cdot}21520m^{-1})$. The results, with possible errors due to possible observational errors, are as follows:—

m.	
2	109790·5 ± 5·6
3	109783·8 ± 12·39
4	109817·7 ± 42·0
5	109836·7 ± 94·5
6	109618·0 ± 220

These numbers require correction to make the values of ν_1, ν_2 correct, viz., 389·19, 190·20. For $m = 2$ the observed values are 388·75, 190·09, *i.e.*, difference of $-{\cdot}44$ and $-{\cdot}10$. Least squares give as the most probable corrections $-{\cdot}33$ to n_1, ·11 to n_2, and ·21 to n_3. This adds a correction of ·6 × possible variation, *i.e.*, 3·3 to the N, making N = 109793·8. Similarly for $m = 3$, ν_1 is ·46 too small and ν_2 is ·33 too small. Treated in the same way a correction of $\frac{10}{17}$ the possible must be added, making N = 109791·1. It is clear that the value of N can easily be constant and = 109790 ± 5 within limits of error. In fact, with this value the errors in λ are respectively about 0, $\frac{1}{2}$, $\frac{3}{5}$, $\frac{1}{2}$, $\frac{3}{4}$ the possible ones. The results are given in the following table:—

	N.	ξ.	μ.	δN.
Zn (5)	109792 (3)	0	·290534	117 (3)
Cd (4)	110022 (2)	0	·359856	346 (2)
Hg (9)	109607 (4)	0	·307463	− 68 (4)
Mg (5)	110457 (3)	− 1	·400856	782
Ca (5)	111406 (4)	− 1	·617130	1737
Sr (4)	111704 (2)	− ·6	·697845	2030
Ba (2)	113023 (3)	− 19	·789911	3348
Al (4)	109267 (4)	0	·238500	− 398
Ga (2)				
In (6)	109348 (6) 109400	0	·277705	− 332 − 175
Tl	109088 109200	0	·247083	− 577 − 475

The numbers after the chemical symbol (*e.g.*, Zn (5)) give the number of lines involved; ξ is a small alteration in the limit $S(\infty)$ as determined from the three first lines of a series. It is unnecessary to give α, as the formula for D_m is $m+1+\mu\,(1-{\cdot}21520m^{-1})$. The slight uncertainty in the last two digits of the number ·21520 will not appreciably modify the result. It is noticeable that the limits in the cases of the Mg group, in which a term m^{-2} was found to be necessary, are close to those found when the series is determined from the first three lines only, and consequently with the term in m^{-1} only. In Hg only nine lines out of the whole known were compared ($m = 2 \ldots 9$ and 12). In all there appear only four exceptions to the rule that the calculated values of N are constant in any one series after the first. They occur in Ca, Sr, In, and Tl. In Ca for $m = 3$ the number is $111458 \pm 8{\cdot}5$ instead of 111406 ± 4. In Sr for $m = 3$ the number is $111779 \pm$? This triplet is interesting as having been missed in K. and R.'s first list of the Sr spectrum and as having been calculated by RYDBERG. The other two exceptions are for In and Tl, in which the values appear to go in two steps, viz., for In 109348, 109348, $109390{\cdot}3 \pm 22{\cdot}6$, 109390, with the two last equal to either within limits of error. If ξ be taken to be -1 they may, however, all be brought to 109343 by allowing the maximum observational errors, but this is scarcely permissible. In Tl $m = 2, 3$ give 109088, $m = 5, 6$ 109200, $m = 6$ either value, whilst $m = 4$ gives 108671. The last is the case mentioned on p. 39, where there is a large error between calculated and observed, and in which a transcription error is suggested. If the value given by the original formula is used, the value for N becomes 109134. Here also, with a small change in the limit, the value of N may be made the same, but only at the expense of allowing maximum errors. It is probable the two last cases correspond to a real change. It is to be noted that, mercury excepted, all the elements of Group II. show a greater value than RYDBERG'S constant 109675, whilst those of Group III. show a less value. The generality of the rule is striking, but a further discussion must be postponed until the atomic weight terms are considered. It does not, of course, affect the question of the atomic volume terms considered above, as the reasoning there is based on the first terms of the series, in which N retains the normal value. It may be noted that this change of N gives the ratio $\alpha\mu^{-1} = {\cdot}21520$ for *all* the elements, and explains why the rule to deduct $W(1-m^{-1})$ always failed for the elements of large atomic weight.

The Principal Series.—No principal series were known in the 2nd and 3rd group of elements until PASCHEN* discovered those of Zn, Cd, Al, Tl and suggested certain lines in those of Mg, Ca, and Hg. Those for the first four were clear and definite, and little doubt could be felt as to the correctness of their identification as a whole. The same certainty cannot be felt as to those for Mg and Ca, and, in fact, I give below certain considerations which tend to throw doubt on some of them. The first definite observations of the HgP are due to MILNER,† who gave the lines of orders 5 to 16. For 5 to 8 he gave values for P_1 and P_2 but, as later work of PASCHEN has shown, he allocated the P_2 lines to the real P_1 and his P_1 lines do not come into the direct line of the series, although it is possible they may be collaterals. Since then PASCHEN‡ has published a long list of lines observed by WIEDMANN, and has attempted

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* 'Zur Kenntnis ultraroter Linienspectra,' 'Ann. der Phys.,' 29 (1909).

† "The Series Spectrum of Mercury," 'Phil. Mag.,' XX. (1910).

‡ 'Ann. d. Phys.' (4), 35.

to complete the series. It is, however, difficult to be certain as to any identification proposed, as there is a maze of lines in this portion of the spectrum. Below I propose certain changes in his identification, for reasons which will be given.

If we now discuss the series for Zn, Cd, Al, and Tl we find that the limits of the series, as found from the lines as a whole, agree very closely with the values of VS (1), but the calculated values of VP (1) deviate very considerably from the values of S (∞). This is in agreement with the deduction already drawn that the S series depend on what was called the *p*-sequence in Part I., and the P series on the *s*-sequence. When, however, we attempt to find the constants μ and α in the usual way we get formulæ which reproduce the lines with fair accuracy in the case of Zn only. It is possible to modify the form so as to get good agreement within observational errors, but it seems preferable to proceed in another way and attempt to discover the connection between the P_1, P_2, and P_3 terms and the relationship which undoubtedly exists between the S and P series by direct comparison of their values. Such relationship will most probably show itself between the values of corresponding denominators. The values obtained, on the supposition of constant N, are given below. For comparative study the corresponding numbers are given for the alkalies.

As in previous cases figures in brackets after a number give the greatest possible variations in the last digits of the number, so far as the variation depends on errors of observations. Other systematic variations may enter by the possible changes in the limits P (∞) or S (∞). With the exception of the alkalies the values for S are calculated from the formulæ (see Table I.). Then VS (1) (or *p* (1)) is taken to be P (∞), and using this as the limit the denominators for the P lines are calculated direct from their observed values. This method, therefore, assumes the validity of the relation P (∞) = *p* (1) = VS (1). In the cases in question, as we have seen, this has always been found to be the case. In the case of the alkalies, however, one of the relations indicated does not hold unless we use the limit found directly from the series (see Table II., Part I.), and that accordingly has been done. Since, however, the top lines in the alkalies are so ill determined the value of P (∞) is used for VS (1). CsS (2) is so uncertain that the value from the formula is also inserted. RbS (2) is also from the formula, as BERGMANN's observed value is very considerably in error. The difference between corresponding numbers are entered between them.

Arranged in this way a number of facts emerge at once. Regarding Zn, Cd, Al, and Tl, they all with one or two exceptions clearly indicate a general law that from $m = 2$ onwards the denominators for the different triplets or doublets in each element differ by the same amount, and that this amount is somewhere about ·7 to ·8 times the corresponding difference for $m = 1$, which gives the values of Δ_1, Δ_2, or the atomic weight terms. We may feel justified, therefore, in using this as a test to apply to PASCHEN's allocation of the upper lines of the P series for Hg. The values

TABLE III.

Zn.

P_3	1·588669 (4)	2·748325 (36)	3·774784 (9)	4·784770 (30)	5·789948 (62)	6·792134 (570)
	3474	**2525**	**2414**	**2375**	**2283**	**2788**
P_2	1·592143 (3)	2·750850 (28)	3·777198 (9)	4·787145 (30)	5·792231 (62)	6·794922 (570)
	7209	**5355**	**5191**	**5154**	**5026**	**5343**
P_1	1·599352 (2)	2·756205 (19)	3·782389 (9)	4·792299 (30)	5·797257 (62)	6·800265 (570)
		528306	**524910**	**524960**	**524988**	**525038**
S_1		2·227899 (6)	3·257479 (83)	4·767339 (240)	5·272269	6·275227

P (∞) = 22096·29

Cd.

P_3	607869 (5)	784277 (25)	813109 (1137)	825854 (25)	831951 (57)	
	10368	**6980**	**6461**	**6407**	**6249**	
P_2	618237 (5)	791257 (25)	819570 (700)	832261 (28)	838200 (57)	
	23109	**17423**	**18269**	**17109**	**17160**	
P_1	641346 (4)	808680 (25)	837839 (222)	849370 (26)	855360 (57)	858125 (205)
		526358	**522077**	**522459**	**522874**	**522294**
S_1		282322 (0)	315762 (80)	326911 (120)	332486	335831

P (∞) = 21054·39

Hg.

P_3	535163	748179	764993	781676	793655	793650
	30002	**24779**	**23817**			
P_2	565165	772958	788810	**96518**	**96451**	**96760**
	87815	**71967**	**71364**			
P_1	652980	844925	860174	878194	890106	890410
		603628	**584737**	**591377**	**597599**	**594489**
S_1		241297	275437	286817	292507	295921

P (∞) = 21832·78

TABLE III. (continued).

				Al.		
P_2	507300	675177 (78)	701930 (23)	711820 (48)		
	1751	**1329**	**1377**	**1380**		
P_1	509051	676506 (78)	703307 (23)	713200 (48)	719220	
		489330	**484456**	**483791**	**484532**	
S_1		187176	218851	229409	234688	237855
			P(∞) = 22926·65			
				Tl.		
P_2	492090	694690	727011	739157	743478	759420
	134154	**94018**	**91195**	**90615**	**92157**	**85635**
P_1	626244	788708 (35)	818206 (15)	829811 (30)	835635	835780
		594887	**589176**	**589045**	**589001**	**585635**
S_1		193821	229030	240766	246634	250155
			P(∞) = 22786·01			
				Na.		
P_2	2·116161	3·132020				
	741	**770**				
P_1	2·116902	3·132790 (38)	4·138086 (200)	5·140442 (865)	6·142040 (1584)	
	490162	**490198**	**491053**	**491219**	**492503**	
S_1	1·626740	2·642592	3·647033	4·649223	5·650537	
				K.		
P_2	2·231690 (200)	3·262250 (28)	4·272653 (89)	5·277685 (200)	6·278840 (1174)	
	2939	**2975**	**2990**	**3167**	**2593**	
P_1	2·234629 (200)	3·265225 (28)	4·275643 (89)	5·280852 (200)	6·281433 (1174)	
	·464597	**·464325**	**·465725**	**·466967**	**·465168**	
S_1	1·770032	2·800900 (64)	3·809918 (267)	4·813885 (76)	5·816265 (475)	

			Rb.			
P_2	2·278956 (55)	3·316160 (28)	4·328553 (149)	5·334080 (314)	6·334350	7·339014
	12889	**12962**	**12995**	**13699**	**12415**	**12172**
P_1	2·291845 (55)	3·329122 (28)	4·341548 (149)	5·347779 (314)	6·346765	7·351186
	487501	**483147**	**485326**	**486337**	**482227**	
S_1	1·804344 (53)	2·845975 (?)	3·856222 (700)	4·861442 (270)	5·864538 (450)	
			Cs.			
P_2	2·328360 (30)	3·373705 (45)	4·389278 (236)	5·397220 (1090)		
	32492	**32104**	**32155**	**32025**		
P_1	2·360852 (30)	3·405809 (45)	4·421433 (236)	5·429245 (1090)	6·443220	
	491944	**490109**	**487789**	**489611**	**499599**	
S_1	1·868908	2·915700 (3390)	3·933644 (138)	4·939634	5·943621	
		2·921641				
		484168				
			Mg.			
P_3	1·659732					
	414					
P_2	1·660146					
	855					
P_1	1·661001	2·817586 (132)	3·847690 (864)	4·862890 (2616)	5·871649 (5523)	
		·502739	**·501097**	**·504792**	**·507626**	
S_1		2·314847 (6)	3·346593 (46)	4·358098 (125)	5·364023 (280)	
			P(∞) = 20467·39			
			Ca.			
P_3	1·792310	3·055350				
	1368	**963**				
P_2	1·793678	3·056313				
	2792	**1995**				
P_1	1·796470	3·058308 (65)	4·124116 (996) ?			
		·573314	**·599043**			
S_1		2·484994	3·525073	4·540524		
			P(∞) = 16760·56			

of the denominators calculated for his lines, the first line being, of course, taken to be also the first of the S series, are as follows:—

P_3 . .	1·535163	?	3·764993	4·775856	5·780490	6·782813
	30002		**4944**	**18593**	**13165**	**10837**
P_2 . .	1·565165	2·734512	3·769937	4·794449	5·793655	6·793650
	87815		**9763**	**84538**	**96441**	**96760**
P_1 . .	1·652980	?	3·860174	4·878987	5·890106	6·890410

The numbers clearly do not follow the law. It is possible, however, to select a set which do so, but only by supposing that the P_2 lines from $m = 4$ and beyond do not occur. They are given in the table above, where the agreement with the law is evident. PASCHEN also suggests another set for $m = 2$, in which the separations are still more out of order, viz.:

2·734512
13667
2·748179
159052
2·907231

He supports this with a considerable list of combination terms, which, though striking, do not prove that the lines in question belong to the direct P series. In fact, there is evidence that some of these combinations are related to the D series. Further, I hope to show, in the next part, that his $P_1(2)$ here is a collateral of the singlet P series discovered by him and published in the same paper. A comparative list of the lines is given in Appendix II.

A similar rule is seen to hold (as was indeed known from the results of Part I.) in the case of the alkalies, except that here the difference of the P_1 and P_2 is the same for all orders. In this group, it will be remembered, the principal series is based on the p-sequence.

Another law also appears in the relation of the Sharp series to the Principal, viz., that the denominators for the Sharp series of any element are found by deducting a constant value from the corresponding denominator of the Principal series, except that the difference is a greater one for the first term, they are roughly as follows:—

Zn . . ·5283, ·5249; Cd . . ·5263, ·5224; Al . . ·4893, ·4844; Tl . . ·5949, ·5891;
Na . . ·4901; K . . ·4660; Rb . . ·4856; Cs . . ·4880;

a similar arrangement also is shown by the suggested allocation in Hg, viz., ·6036, ·59, an additional evidence in its favour. The differences between P and S in the list do not appear to be rigorously constant after $m = 2$. This can be easily explained by very small changes in the limits $P(\infty)$ or $S(\infty)$. In fact, as has been seen already, RYDBERG'S law does not appear to be quite rigorously exact. PASCHEN'S

2·907231 would make the first number ·6659, and, therefore, quite out of analogy with the others. Again, in the alkalies the same law is seen, with just the same modification as in the previous case, viz., constant for each.

A closer inspection shows that the differences between the P terms cannot be exactly constant after $m = 2$. They seem to descend in two steps instead of one. The general law, however, seems so well established that the cause of the real variation is to be sought. It is possible it may be due to the properties of the atomic weight term. The second law, however, affecting S, P seems to be very closely followed. It should be noticed that the alkalies and Al give differences less than ·5, whereas the others give values greater than ·5. It suggests that the remainder of the Al sub-group, viz., Sc, Y, La, Yb, would also require values less than ·5. If such a rule held for the two sub-groups in each group of the periodic table, we should expect the Mg, Ca, &c., to require values less than ·5. The evidence, however (see below), is rather against this so far as any evidence is available.

In the alkalies the Principal series are formed on the p-sequence, and the subtraction of the respective constants by the second of the above laws gives the first term of the S series as hitherto recognised. The question naturally arises, what becomes of the term deduced in a similar way from the first term of the s-sequence, and do lines exist corresponding to these? If we attempt to calculate them we must know the value of the constant to be deducted. Is it the same as for $m = 2$, which is larger than that for the others, or is it a number larger still? If we use the rough values obtained for $m = 2$ in Table III. and apply them to $m = 1$, the following values of the denominator result:—

Zn . . 1·0710; Cd . . 1·1170; Hg . . 1·0494; Al . . 1·0203; Tl . . 1·0313;

corresponding to lines in the neighbourhood of

	Zn.	Cd.	Hg.	Al.	Tl.
S_3 . . .	1916	2198	1884		
S_2 . . .	1909	2173	1824	1752	1856
S_1 . . .	1896	2119	1682	1748	1622

We should expect such lines, if they exist, to be exceptionally strong. A number of weak lines are known in these regions, but the only strong ones that could possibly belong are the Cd lines—

Intensity.	λ.	n.	
1	2170·11	46066·38 ± 10·6	
			551·26 ± 14
4r	2144·45	46617·64 ± 4·3	
			1076·36 ± 15
3n	2096·1	47694·00 ± 11	

but the nature of the three lines are different and 1076 is about $\frac{9}{10}\nu_1$. The ν_2 should be 542 and the observed is within limits of error. Al has a weak doublet

1	1857·56	53816·42	
			100·66
3	1854·09	53917·08	

The separation is probably within error limits of $\nu = 112$, but is as it stands also about $\frac{9}{10}\nu$. The evidence is therefore against the existence of the terms in question, but the possibility of the lines splitting up into collaterals of smaller intensity, as is the case of HgP, should be borne in mind.

If the Cd triplet is correctly assigned, viz., $n = 47694$, the number to be deducted from the s-sequence should be ·5275 in place of ·5243. This is as much above ·5243 as that is above ·5222.

We may now proceed to consider PASCHEN'S identification of lines for the MgP and CaP series in the light of the regularities discovered above. In applying them it is necessary to decide on the limits to employ, using, at least at first, RYDBERG'S law as to their connection. The limit calculated for MgS from the first three lines gives (see Table I.) 39758·18 ± 1·12, and from the first four (*i.e.*, term in m^{-2}) 39752·83 ± 2·73, from which RYDBERG'S law gives ($\text{MgS}_1(1) = 19285·44$) respectively 20472·74 and 20467·39. The value 39752 agrees best with the measurements of the higher orders, whilst 20464·43 is the actual limit calculated from the three first lines of PASCHEN. Taking then $\text{S}(\infty) = 39752·83$ and $\text{P}(\infty) = 20467·39$, the numbers for comparison are given in the table above, using for $\text{P}_1(2)$ PASCHEN'S bolometer reading (7655·3), as it gives the most favourable comparison. It will be seen that the differences are respectively 2739 (138), 1097 (900), 4792 (2741), 7626 (5803). These by rather forcing the limits of variation can be made to give typical differences of about, say, 2700, 2000. A closer agreement can, of course, be found by allowing RYDBERG'S law to be only approximate. The result of the discussion, therefore, does not contradict PASCHEN'S identification.

In view, however, of the suspicion raised above that the difference for Mg and Ca might be expected to be less than ·5, it will be interesting to see if lines satisfying this can be found. Out of observed lines, however, I have only been able to find two which might fit in with this system, viz., $15768·3 = \text{P}_3(2)$, $15759·1 = \text{P}_2(2)$. These give values of the denominator of ·786281 and ·786645 with a difference 364, fitting in well with that of $\text{P}_3(1)$ and $\text{P}_2(1)$, but there is no appearance of a $\text{P}_1(2)$, which should have a difference of about 4725 over the denominator of S(1).

For Ca PASCHEN gives for the first triplet 19856·9, 19935·8, 19946·8, and for the first of the next triplet 9546·8. Using limits on the same basis as for Mg it is found the $\text{P}(\infty) = 16760·56$, $\text{S}(\infty) = 33983·45$. The first S triplet, which RYDBERG'S law makes also the first of the P, gives separations 2792 and 1368. PASCHEN'S first triplet gives 2600 and 359, which is not in order. If, however, the line 19917·5 observed also by him be taken for P_2, the separations become 1995, 963, and quite in order, being both about ·7 times the first set. In the table above I have, therefore, ventured to insert it in place of his selection, although it coincides with an undoubted D line. The denominator of this triplet is ·5733 above the corresponding one for S. His next is ·6510 above it, which is far out and cannot be made normal by any reasonable change in the limits. If the line 9694·5 be taken the difference becomes ·5990, which is better but still too large. This is the only other available line observed in the neighbourhood, so that it is probable that the first line of the next triplet has not been observed.

Summary.

1. The most important result of the discussion would seem to be the considerable weight of evidence, in addition to that afforded in Part I., that the series lines—at least the Principal and Sharp—depend in a very definite way on a certain physical quantity peculiar to each element which is approximately measured by what is generally understood as its atomic volume. The numerical evidence afforded from a study of the low melting-point elements of the first three groups of the Periodic Table is remarkably exact. The numerous lines of all these series are represented within limits of error, and as a rule with extreme closeness, by the formula adopted. The argument is based on the denominator of $p(1)$, and this is determinable with great exactness; in fact, any possible error in this due either to error of observation or error in the limit chosen for the series will exert practically no influence on the result.* A change in N might do so to some extent. Any uncertainty is due to uncertainty in the values used for the atomic volume, which might amount to as much as 1 per cent., *e.g.*, changing 2740 by 30. The high melting-point elements of Group II. do not show the law with such certainty, but there are clear indications of it. In these elements the type of formula has required a modification, and, in addition, the series are not well developed in the higher members Sr, Ba and Ra. Consequently the limits are not determined with such certainty as in the other cases. Nevertheless Mg and Ca quite fall into line with the others, and even in Ra it is possible to give some indications of the value of the density of the solid metal.

The fact that the terms depend on multiples of atomic volumes as ordinarily calculated may be interpreted in one of two ways. Either that the periods of the vibrating configurations do actually depend on multiples of the essential atomic volumes *or* that multiples do not enter here, but that the packing together of the configurations when they are aggregated into solid masses is closer or less close. *E.g.*, compare Zn with factor 9 and Hg with factor 6. The period of Zn may depend

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* An increase of ξ in the limit of Zn would alter the ratio by $(1 - \cdot 00022\xi)$, and ξ cannot be more than a few units. In the case of Ba only is ξ indeterminate to the extent of so much as 170, and for Ba the corresponding factor is $(1 - \cdot 00013\xi)$, large enough to require a change in the multiple of ν.

on 9 times its volume constant, and Hg on 6 times its corresponding volume constant. On the other hand, Zn and Hg may depend on their volume constants in the same way, but the centres of the Zn molecules be packed 9 times more closely together than in the normal case, and the centres of the Hg molecules 6 times. On the first view the multiples depend on the internal configuration of the atom, on the second on the configurations of the molecules in gross matter, in other words, on the value of the ratio atomic weight to density. If the first interpretation is correct, we might expect to find other series in an element depending on other multiples. I am not sure that I have not observed indications of such, but it will require further search before a definite reply can be given. On the second interpretation no such additional lines can be expected.

2. Additional evidence to that obtained in Part I. has been afforded of the existence of a universal constant, approximately ·21520, which gives the ratio of α/μ in the p-sequence $\mu+\alpha/m$, and also in the s-sequence if certain relations indicated between the s- and p-sequences are found to be exact. This constant must be a pure number* in contradistinction to N, which is of the dimension $(\text{length})^{-1}$.

3. A comparison of the denominators of $VP_1(m)$, $VP_2(m)$, $VP_3(m)$ has indicated that whilst in the alkalies they differ by the same amount in the same element for all orders, in the 2nd and 3rd groups the difference proceeds in two steps, viz., that after the first order the remaining differ by the same amount, and that this is about ·7 times the difference for $m = 1$. Further, a comparison of the above with $VS(m)$ shows that a similar law holds between the denominators of $VS(m)$ and $VP(m)$. These laws are applied as a criterion to the lines allotted by PASCHEN for HgP, MgP, and CaP, and, in consequence, certain modifications are suggested.

4. It is found in the 2nd and 3rd groups, in opposition to the rule in the first, that the S series follows the p-sequence and the P series the s-sequence.

5. An attempt is made to arrange the S and D series for Europium and Radium. Eu is found to fit the gap between Cd and Hg and a density 12·58 deduced for it. The density of Ra should be $1·02x$, where x is probably 5 or 6.

APPENDIX I.

The S *and* D *Series of Europium.*

The only published spectra of Europium are the arc and spark spectra of the ultra violet lines by EXNER and HASCHEK. CROOKES† has observed, but not published, its spectrum, but remarks that the Europium used by EXNER and HASCHEK must have contained several impurities. EXNER and HASCHEK'S list of arc lines contains over

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* $2/(3\pi) = ·21511$.

† "On Europium and its Ultra-Violet Spectrum," 'Roy. Soc. Proc.,' 74, p. 550 (1905).

500 lines shorter than 4698. A photograph of a portion of the longer wave-length, kindly given me by Sir W. Crookes, contains a few faint lines above Exner and Haschek's limit, as well as a few others not given by the latter.

Scandium and its group, Yt, La, Yb, show doublet series.* On the contrary, Europium, with which they are associated, has a spectrum of triplets with separations 2632 and 1004. Moreover, when expressed as fractions of the square of the atomic weight (152·03),† these are found to be in correspondence with those for Cd and Hg, and therefore suggest that Eu is the member wanting in the Periodic Table between those elements; if so, we should expect to find the corresponding S and D series, which are well developed in Cd and Hg, as well as other peculiarities. Unfortunately, however, the first line $S_1(1)$ and $S_2(1)$ should come about 5400 if they are similar to Cd and Hg, and this region is outside the published lists.

It is possible, however, to allocate observed lines to fit the conditions for the S and D series. They are given in the following lists:—

Sharp Series.

	λ.	n.	ν.
m = 1	(5379·1)‡	(18585·5)	**2632·5**
	(4711·69)‡	(21218)	**1004**
	4498·81	22222·00	
m = 2	3322·01	30093·73	**2629·42**
	3055·07	32723·15	**1001·38**
	2964·35 spark	33724·53	
m = 3	2909·10	34365·08	**2633·86**
	2701·99	36998·94	
m = 4	2744·36	36427·75	**2634·60**
	2559·30	39062·35	
m = 5	2659·50	37590·17	
m = 7	2577·69	38783·00	

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* Discussion deferred to a later communication.

† Jantsch, 'C. R.,' 1908.

[‡ See note at end.]

DIFFUSE SERIES.

	λ.		n.			ν.	
m = 2	3637·84	spark	27480·99	**2630·69**	30111·68	**1004·13**	31115·81
	3638·22		27478·27	**2633·41**			
	3629·94		27541·00	**2630·45**	30171·45		
	3619·97		27616·83				
	3320·03						
	3313·46						
	3212·89						
m = 3	3004·9	spark	33269·45	**2632·45**	35902·00	**1002·45**	36904·45
	3001·48		33307·36				
	2708·91	spark					
m = 4	(2787)		(35869·76)	**2632·5**	38502·26		
	(*2786*)		*35881·25*				
	2596·49	spark					
m = 5	2683·29	spark	37258·85	**2632·5**	(39891·35)		
	2682·72		37264·77				
	(2506)						
m = 6	(2624·72)		(38088·08)	**2632·5**	40720·59		
	(*2624·36*)		(*38093·38*)				
	2455·03						
m = 7	(2588·18)		(38625·87)	**2632·5**	41258·37		
	(*2587·96*)		(*38629·12*)				
	2423·03	spark					
m = 8	2564·27		38986·05	**2648·07**	41634·22		
	2401·15	spark					
m = 9	2387·41	spark			41873·94		

The first two λλ for S 5379·1 and 4711·69 are extrapolated from the observed faint line 4498 by taking $\nu_1 = 2632{\cdot}5$ and $\nu_2 = 1004$, which is about the mean value of the ν's. Several other alternatives might be taken, but this gives the best analogy with Cd and Hg. The first three lines give for the formula

$$n = 40364{\cdot}08 - \mathrm{N}/\{m + 1{\cdot}291603 - {\cdot}047520m^{-1}\}^2$$

with errors for $m = 4, 5$ of ·14 and ·36, probably within any observational error. The values of the Δ come out (with $\nu_1 = 2630{\cdot}5$ and $\nu_2 = 1004$) to

$$\Delta_1 = {\cdot}051222 = {\cdot}022162w^2,$$
$$\Delta_2 = {\cdot}018327 = {\cdot}007929w^2.$$

Δ_2 is intermediate to those for Cd and Hg, viz., $\cdot008208w^2$ and $\cdot007500w^2$ respectively, but for the latter Δ_1 are $\cdot018289w^2$ and $\cdot021953w^2$, so that Δ_1 for Eu is a slightly larger multiple of w^2 than for Hg, supposing that the atomic weight of Eu is correctly given as 152·03.

The ratio $(\alpha+\mathrm{W})/(\mu+\mathrm{W})$, which ought by analogy to be ·21520, is ·21246. But the uncertainty of the top line might account for this: *e.g.*, if this supposed line be taken 2·2 A.U. greater this ratio would be ·21520 with $\mu+\mathrm{W} = {\cdot}310572$.

There is some appearance of a satellite series for EuS., viz., the lines whose wave numbers are

$$\left.\begin{array}{ll} \mathrm{S}_{12}(1) & (18516{\cdot}60) \\ \mathrm{S}_{22}(1) & (21150) \end{array}\right\} \text{based on } 22155{\cdot}46,$$
$$\mathrm{S}_{12}(2) \quad 30090{\cdot}02 \quad \mathbf{2633{\cdot}13} \quad 32723{\cdot}15.$$

These give the formula

$$40361{\cdot}90 - \mathrm{N}/\{m + 1{\cdot}294528 - 053875m^{-1}\}^2,$$

in which the calculated values of λ for $m = 4$ and 5 differ from the observed by ·12, ·41. The limit is so close to the former that they may be taken as coincident, indicating, therefore, that the lines are satellites as ordinarily understood. There appear, also, to be series associated with these. For instance, writing the wave numbers, with separations,

S_1.	ν_1.	S_2.	ν_2.	S_3.
{ (18858)*	**2633**	21491·37 (1+)	**998**	22489·34 (1)
or (18856)*	**2630**	(21486)	**1003**	22489·34 (1)
30090·02 (3)	**2633·13**	32723·15 (4)	**1001·38**	33724·53 (1+) spark
34365·08 (3)	**2633·86**	36998·94 (4)		
36440·76 (2)				
37604·15 (1+)				
38325·24 (2) spark				
38789·61 (2)				
39128·98 (1) spark				

the numbers in brackets denoting intensities.

[* See note at end.]

With 18856 for the first line the first three give

$$n = 40397{\cdot}87 - \mathrm{N}/\{m+1{\cdot}267384-{\cdot}010971m^{-1}\}^2,$$

and the differences of λ from the observed for $m = 4, 5, 6, 7, 8$ are respectively $-{\cdot}01$, $-{\cdot}02$, $-{\cdot}34$, $+{\cdot}20$, $-{\cdot}54$. The last possibly does not belong to the series.

The agreement is good and the extrapolation is made on an observed pair S_2 and S_3, so that there is a temptation to take it as the real S series. The μ and the α are not, however, analogous to those of Cd and Hg, and the ratio $(\alpha+\mathrm{W})/(\mu+\mathrm{W})$ is about ·1 instead of ·215.

The following lines also give a parallel series :—

S_1.	ν_1.	S_2.	ν_2.	S_3.
(19913·0)	**2633·80**	22546·80 (1+)	**1004·39**	23551·19 (2)
30171·45 (2)				
31626·68 (5)	**2635·05**	39061·73 (1).		

The first is extrapolated as before by ν_1 only. The second has no observed lines for ν_1 or ν_2, the magnitudes seem in wrong order, and no other orders have been observed. Little weight can therefore be given to it. But the formula is

$$40440{\cdot}60 - \mathrm{N}\,\{(m+1{\cdot}379503-{\cdot}068050m^{-1}\}^2,$$

with a limit about half way between those of Cd and Hg, and with a ratio $(\alpha+\mathrm{W})/(\mu+\mathrm{W}) = {\cdot}21703$. Moreover, the ν_1's associated with the three series show an increase with the limit, as should occur. For instance, $\Delta_1 = {\cdot}051160$ would give respectively 2629, 2631, 2635 for limits 40364, 40397, 40440. This is quite in accordance with the general constitution of spectra.* The abnormal intensities may be due to the kind of instability referred to above.

The D series has been filled up by using spark lines where arc were wanting. If, as we suppose, Eu is analogous to Hg, the spectrum taken from the salt on the carbon arc might be expected to partake somewhat of the nature of a spark spectrum. To get a spectrum analogous to the simple spectrum of Hg use should be made either of the arc *in vacuo*, or with the salt in a vacuum tube. In addition, it is reasonable to expect that the wanting elements throughout the horizontal row in the Periodic Table might show a greater amount of instability in the molecular groupings than the corresponding elements in the vertical groups. I hope to show in a future communication that there is direct evidence of such re-groupings in other spectra, and that we can obtain indications of their nature. If the grouping peculiar to a particular series is subject to an excessive disrupting force in the production of the spectrum, a few only will survive, and consequently the line observed will be faint,

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* "On the Dependence of the Spectrum of an Element on its Atomic Weight," 'Brit. Assoc. Reports,' 1911 [p. 342].

and others be observed displaced according to certain laws. The matter is far too large to deal with here and will require a paper to itself. I mention it here, however, in order that judgment may be suspended if any natural doubt is felt concerning the small intensities of the series, the mingling of the arc and spark lines, and the various lacunæ which appear. That lacunæ actually do occur in EXNER and HASCHEK'S list is shown by the absence of the line 4552·6 from the arc, its appearance as a weak line in the spark, whilst it is of considerable strength in CROOKES' photograph.

In the list of D lines those in brackets have not been observed. They are either D_{12} lines deduced from D_{21}, or D_{21} deduced from D_{12}. The lines in italics are those calculated from the formula for D_{11}. The values of D_{11} and D_{12} gradually converge, as they should do, their differences being

75·83, 37·91 ?, 11·49, 5·92, 5·30, 3·25.

There may be some doubt whether the series generally assigned to the diffuse for Zn, Cd, Hg are really diffuse. The α term is negative, and agreement within observational errors is obtained only by using $m-{\cdot}5$ instead of m, but they are clearly of the same type for all these elements. The formula for Eu was therefore taken of this form. The constants were determined by using the same limits as for S, viz., 40364·08, and only the *two* first lines. The result for D_{11} is

$$n = 40364{\cdot}08 - N/\{m + {\cdot}956046 - {\cdot}068460/(2m-1)\}^2.$$

D_{21} is determined from this by finding the difference between the μ's for the first line of D_{11} and D_{12}. This is practically the same as $\Delta_1/6$, and the altered μ is used for the calculation of the succeeding values. The table gives the difference between the observed and calculated values, on the supposition that ν_1 is 2632·5. The third column is the result if ν_1 be taken as 2633. As throughout the paper, * denotes a line used for calculation.

m.	D_{11}.	D_{21}.	D_{21}.
2	*	*	*
3	*	·53	
4		− ·29	− ·25
5	− ·02	− ·22	− ·18
6		− ·02	·00
7		− ·03	·00
8	·60	− ·52	− ·49
9		+ ·76	+ ·79

(The last two are probably not the real lines.)

In this note I am not going into the question of the constitution of the Europium spectrum in general. Indeed, the list of triplets with separations 2630 and 1004 is a very long one, and, in addition, there are the usual narrow triplets depending on the D satellites. As an example of a strong triplet the following set may be taken, all of intensity 50 on Exner and Haschek's scale:

λ.	n.	ν.
·4435·74	22537·95	
		2630·30
3972·16	25168·25	
		1003·87
3819·80	26172·12	

The S *and* D *Lines of Radium.*

Judging from the falling off both in intensity and number of the S and D lines as we pass from Mg and Ca to Sr and Ba, it might be expected that the corresponding series for Ra—two places farther on in the Periodic Table—would be difficult to allocate even if they were present at all. The difficulty is increased the more because the only spectral measures published are those of the spark, in which these series are always weakened. Spark spectra, in general, show a greatly increased number of lines which are related to one another in quite definite ways and many related to series lines. This makes the search for doublets much more difficult, as there exist whole series of doublets with separations slightly different from one another. This necessitates a complete study of the whole spectrum in order to feel complete certainty in any allocation of lines to a series, unless such series is clearly marked by many terms. There is, therefore, some degree of uncertainty in the allocation proposed below, in spite of the evidence adduced in its favour.*

The most complete and reliable measurements of the spectrum are those of Runge and Precht,† between 6487 and 2709. Their plates were only sensitive up to 6500. In addition, Exner and Haschek publish tables both for the arc and spark, but their material can hardly have been pure. They give comparatively few lines, and probably not so reliable as their other lists.

Even in Runge and Precht's work it is probable that most of the lines which would be comparable with the weaker ones in the Ba lists have not been observed. The result is that it is not so easy to allocate the D series, as the separations result from a pair of lines the second of which is strong and the other is a not observed weak satellite of the first. In consequence we shall get separations less than the true ν_1 and ν_2, and this is exemplified in the list which follows. The wave-numbers only are given—the wave-lengths will be found in Appendix II.

$$\nu_1 = 2050{\cdot}27, \qquad \nu_2 = 832{\cdot}00\,?$$

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* There is also some additional evidence drawn from their relation to other lines, of a similar nature to that referred to under Europium.

† 'Ann. der Phys.,' 14, p. 419.

THE D SERIES.

$m = 3$	(16107·45)	**2050·27**	18157·72 (4)	**832·00**	18989·71 (6)
	12·31		12·31		
	(16119·76)	**2050·27**	18170·03 (8)		
	3·34				
	16123·10 (10)				
$m = 4$	(18510·67)	**2050·27**	20560·94 (2)		
	1·75				
	18512·42 (8)				
$m = 5$	19804·02 (1)				
$m = 6$	(20582·97) (λ = 4857·05) ? hidden by λ = 4856·25 (8)				
$m = 7$	21089·93 (2)				
$m = 8$	21438·12 Exner and Haschek's arc.				

THE S SERIES.

$m = 3$	(14728·20)	**2050·26**	16778·46 (10)	**882·05**	17660·51 (10)
$m = 4$	17846·78 (8)	**2050·27**	19897·05 (1)		
	17879·71 (1)	**2043·50**	19923·21 (4)	**890·95**	20814·91 (2)
$m = 5$	(19440·00)	**2050·22**	21490·22 (1+)	Exner and Haschek's arc.	

In the above the figures in brackets after the wave-numbers represent intensities; the wave-numbers in brackets are those of unobserved lines, put in partly to illustrate the arrangement of satellites.

The lines 16107, 16119 (λλ = 6206·6, 6201·9) would be in the region where the photographic plates were insensitive; in fact, the measured lines here are of intensity 4 at least, whereas λ = 6206·6 would certainly be less (by analogy), but 6201·9 (by analogy) ought to have been seen if it existed, unless overshadowed by the very strong line 16123 (λ = 6200·3). 18510 would certainly be of small intensity, probably less than those actually measured, but the convergence (3·34) and (1·75) of the two satellites of the lines looks correct. If $D_{13}(3)$ is correctly allotted and $\nu_2 = 882$, there must be a satellite $D_{23} = 18107·66$. Its distance from $D_{22} = 50$, which lies in order with 12·31 and 3·34.

In the S 14728 (λ = 6787·86) is extrapolated. The next set ($m = 4$) appear to show satellites. It may be noted that an alteration of 7 in $S_2(4) = 19923$ brings both ν_1 and ν_2 into order. The strong line 17846 has been used in the calculation. Exner and Haschek give 21490·22 in the *arc* as a weak line and 19440·58 is extrapolated from this. The value calculated from this formula in m^{-1} is 19430·58, and from analogy with Ba and Sr the true value should be expected to be somewhat larger than this. It should be noted that it is outside EXNER and HASCHEK's region of observation; 21490 may possibly, therefore, be a correct identification for $D_{21}(5)$.

The first three D_{11} lines ($m = 3, 4, 5$) give the formula

$$n = 22760{\cdot}09 - \mathrm{N}/\{m + 1{\cdot}130149 - {\cdot}195236m^{-1}\}^2.$$

This gives the following values of obs.−cal. of λ for the next three ($m = 6, 7, 8$), viz., −·78, −·11, −·17. The first is too large for an observational error, and the true line is possibly hidden by the strong line 4856, but there may possibly be another explanation which would at the same time make the others in still better agreement, and bring into relation with the series the strong lines 5041·52 (6), 4856·25 (8). As this depends on the relations of the atomic-weight terms to D series its discussion must be deferred. The object at present is to determine the limit, which cannot be far from 22760·09. This should also be the limit for the S series. Using this with the two first suggested lines* for S_1, *i.e.*, (14728·20) and 17846·78, the resulting formula for S_1 is

$$n = 22760{\cdot}00 - \mathrm{N}/\{m + 1{\cdot}783424 - {\cdot}176286m^{-1}\}^2.$$

The separations $\nu_1 = 2050{\cdot}27$, $\nu_2 = 832{\cdot}00$ now give $\Delta_1 = {\cdot}092658$ and $\Delta_2 = {\cdot}034390$, but there is some doubt about ν_2. With this value of Δ_2 the denominator of the formula may be written

$$m + 1 - \Delta_2 + {\cdot}816780\,(1 - {\cdot}21582m^{-1}),$$

in very close analogy with the other cases.

APPENDIX II.

The S *and* P *Series Lines of the* 2nd *and* 3rd *Groups of the Periodic Table.*

Mg.			Ca.		
S_1.	S_2.	S_3.	S_1.	S_2.	S_3.
(2) 5183·84	5172·87	5167·55	(2) 6162·46	6122·46	6102·99
3336·83	3332·28	3330·08	3973·89	3957·23	3949·09
2942·21	2938·67	2936·99	3487·76	3474·98	3468·68
2781·53	2778·36	2776·80	3286·26	3274·88	3269·31
2698·44	2695·53	2693·97	3181·40	3170·23	3166·95
2649·30	2646·61	2645·22	3117·74	3107·96	3101·87
MgP 15028·3, 7656·6 ± 1, 6315·6, 5783·4			19856·9 CaP = 19917·5, 9694·5 ? 19946·8		

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* This is the same as finding S_2 from the actually observed lines allocated to S_2.

Sr.			Ba.		
S_1.	S_2.	S_3.	S_1.	S_2.	S_3.
(2) 7070·7	6878·8	6791·4	(2) 7906·13	7392·83	7195·71
4438·22	4361·87	4326·60	4903·11	4700·64	4620·19
3865·59	3807·51	3780·58	4239·91	4087·53	4026·57
3628·62	3577·45	3553·7	3975·55		
3504·70	3456·78	3434·95	3841·72		

Ra.		
S_1.	S_2.	S_3.
(3)	5958·4	5660·81
(4) 5601·72	5024·5	
5591·4	5017·9	4803·1
	? 4652·0	

Zn.					
S_1.	S_2.	S_3.	P_1.	P_2.	P_3.
(2) 4810·71	4722·26	4680·38	(2) 13054·89	13151·50	13197·79
3072·19	3035·93	3018·50	6928·58	6938·73	6943·47
2712·60	2684·29	2670·67	5772·22	5775·64	5777·24
2567·99	2542·53	2530·34	5308·71	5310·31	5311·04
2493·67	2469·72	2457·72	5068·71	5069·67	5070·16
2449·76	2427·05	2415·54			

Cd.					
S_1.	S_2.	S_3.	P_1.	P_2.	P_3.
(2) 5086·06	4800·09	4678·37	(2) 13979·22	14327·99	14474·62
3252·63	3133·29	3081·03	7346·10	7382·49	7396·58
2868·35	2775·09	2733·97	6099·31	6111·68	6116·35
2712·65	2629·15	2592·14	5599·11	5604·99	5607·09
2632·29	2553·61		5339·71		
2582·86	2507·93	2474·15			

Eu.

S_1.	S_2.	S_3.	The second series.		
(2) (? 5379·1)*	(4711·69)*	4498·81*	(5301·5)	4651·75	4445·33
3322·01	3055·07	2964·35	3322·42	3055·07	2964·35
2909·10	2701·99		2909·10	2701·99	
2744·36	2559·30		2743·38		
2659·50			2658·51		
			2608·47		
2577·69			2577·25		
			2554·90		

[* 5381·46, 4713·77, see note at end.]

Hg.

S_1.	S_2.	S_3.	P_1.	P_2.	P_3.
(2) 5460·97	4358·56	4046·78	(2) 12071·32	13208	13674·32
3341·70	2893·67	2752·91	6907·78	7044·27	7092·456
2925·51	2576·31	2464·15	5804·28	5838·99	5868·30
2759·83	2446·96	2345·41	5354·240		5384·901
2674·99	2380·06	2284·2	5120·830		5138·26
2625·24	2340·60		4981·00		4991·7
2593·43	2314·7	2224·7	4890·45		4897·1
2571·85	2284·2		4827·3		4832·4
2556·36	2284·2		4782·3		
2545·09	2275·5		4748·3		
(2536·36)			4723·0		
2529·47			4702·0		
2524·48			4685·5		
			4672·9		
			4662·6		
			4653·6		

Al.

S_1.	S_2.	P_1.	P_2.
(2) 3961·68	3944·16	(2) 13125·36	13151·65
2660·49	2652·56	6696·27	6698·94
2378·52	2372·21	5557·28	5558·17
2263·83	2258·27	5107·5	
2204·73	2199·71		

Ga.		In.	
S_1.	S_2.	S_1.	S_2.
(2) 4172·25	4033·19	(2) 4511·44	4101·87
2780·28	2718	2932·71	2753·97
2481·1		2601·84	2460·14
		2468·09	2340·30
		2399·33	2278·3
		2357·7*	2241·6
		2332·2	2218·3
			2200·0 ?
		* ? 8·7	2191·2

Tl.			
S_1.	S_2.	P_1.	P_2.
(2) 5350·65	3775·87	(2) 11513·22	13013·8
3229·88	2580·23	6549·99	6713·92
2826·27	2316·01	5528·118	5584·195
2665·67	2207·13	5109·65	5137·01
2585·68	2152·08	4891·3	4906·5
2538·27	2119·2	4760·8	4768·7
2508·03	2098·5	4678·3	
2487·57	2083·2	4617·4	
2472·65	2072·4	4574·8	
2462·01			
2453·87			
2447·59			
2442·24			

The lines for MgS and CaS were first allotted by RYDBERG* in his original memoir presented on November 13, 1889, to the Swedish Royal Academy. The values are the observations of KAYSER and RUNGE (' Ann. d. Phys.' (3), 43, p. 387, 1891). In the same paper KAYSER and RUNGE observed Sr (2, 4, 5), but they were arranged in the series by RYDBERG (' Ann. d. Phys.' (3), 50, p. 629), who pointed out that there ought to be a set 3865·39, 3807·37, 3780·47, and that they were probably hidden by strong Cyanogen bands. This was afterwards fully confirmed by K. and R. (' Ann. d. Phys.' (3), 52, p. 115). The first lines of the series were first observed by LEHMANN (' Ann. d. Phys.' (4), 8, p. 647, 1902), but the more accurate values of SAUNDERS (' Astro. Phys. Jour.,' 32, p. 170) are inserted in the list. In the case of Ba the second triplet and the first of the next two were observed by K. and R., but

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* ' Kongl. Svensk. Vetens. Akad. Hand.,' Bd. 23, No. 11. In this memoir, which laid the foundation of what is known as to series relationships, the material is chiefly due to the observations of THALÉN, of HARTLEY and ADENEY, and of LIVEING and DEWAR.

the series was first arranged by SAUNDERS ('Astro. Phys. Jour.,' 28, p. 223), who completed the list by the addition of the three lines $S_{23}(3)$, $S_1(5)$. The highest triplet was observed as in Sr by LEHMANN, but the numbers given in the list are those of HERMANN ('Ann. d. Phys.' (4), 16, p. 698).

In ZnS the first three triplets were allocated by RYDBERG (*loc. cit.*). The list was completed by K. and R., and their measures for the whole are inserted. We owe the discovery of ZnP to PASCHEN ('Ann. d. Phys.' (4), 29, p. 644).

In CdS, again, RYDBERG gave the first two triplets, and the first two lines of the next, whilst K. and R. gave the remainder. They also gave 2521·74 for $S_3(5)$, but it must be wrong, for it gives a separation from $S_2(5)$ of 494·77 instead of 541·90. It is, therefore, 3 A.U. too small. $S_1(6) = 2582{\cdot}86$ makes $\nu_1 = 1156{\cdot}38$ instead of 1171·00. CdP is due to PASCHEN (*loc. cit.*), but the values inserted after the first are the later ones of PASCHEN and WIEDMANN ('Ann. d. Phys.' (4), 35). For Eu see Appendix I.

In HgS RYDBERG arranged the first three triplets, KAYSER and RUNGE added the fourth and the first line of the fifth. The remaining lines, $m = 6$ to 13, of HgS were observed and arranged by MILNER ('Phil. Mag.' (6), 20, p. 636). The lines $S_2(5, 6)$ observed by STILES ('Astro. Phys. Jour.,' 30, p. 48), $S_3(5)$, $S_2(9, 10)$ observed by HUFF ('Astro. Phys. Jour.,' 12, p. 103), $S_2(7)$ EXNER and HASCHEK, $S_3(7)$ EDER and VALENTA have been inserted by the writer. They give for the fifth triplet $\nu_1 = 4630{\cdot}80$, $\nu_2 = 1762{\cdot}59$. $S_2(6)$ gives $\nu_1 = 4630{\cdot}7$. The seventh triplet gives 4641·4 and 1747·0; a slight error in $\lambda = 2314{\cdot}7$ would put both these right. $S_2(9, 10)$ make respectively $\nu_1 = 4659{\cdot}1$, 4653·3, but the former is identical with $S_3(5)$. There may be some doubt about $S_2(7)$ and $S_3(7)$, as they are both spark lines, and $S_3(7)$ is rather too strong, but there can be little doubt about the others. For $S_1(5)$ the measurement of STILES is inserted in place of that of K. and R., as it was observed under better conditions. For the HgP PASCHEN made an unsuccessful attempt to locate the first triplet in the same paper as that in which he published the results for the other P series, referred to in the text. The series was first determined as to its lower orders $m = 4$ to 15 by MILNER (*loc. cit.*), then PASCHEN and WIEDMANN observed the same set up to $m = 16$, and attempted to settle the position of the top lines. In the list above, the arrangement is given as modified in the text (p. 54).

In the third group of elements the P lines have been observed and allocated by PASCHEN ('Ann. d. Phys.' (4), 29). 5105, as observed by him, was the edge of a band, and, as pointed out by him, was too strong to be AlP (4), although it should be close to it. Since then MANNING, working in my laboratory, has found a very faint line at 5107·5, which is doubtless the line in question. RYDBERG in his original memoir gave the five doublets of the AlS series, and at the same time suggested four others. The S and D lines here, however, come so close together that with the inexact values at his disposal his arrangement of these last is now seen to be incorrect. As in other cases, we owe to KAYSER and RUNGE ('Ann. d. Phys.' (3), 48, p. 143) more correct measures, which at the same time established RYDBERG'S selection of the first five.

Some doubt may be felt about the lines adopted for GaS. In his memoir RYDBERG used certain regularities he had noticed amongst other series to deduce what the Ga series ought to be—adopting the doublet 4172, 4033 for S_1 and S_2. He calculated 2747 and 2436 for the two next lines in S_1 and 2966, 2505 for the D lines. Since then EXNER and HASCHEK have published their spark and arc measurements. KAYSER in his 'Spectroscopie'—no doubt guided by RYDBERG'S calculations, as there was nothing else to go upon—allotted E. and H.'s spark line 2780·28 to RYDBERG'S supposed 2747, with 2719·76 (arc) as the second of the doublet ($\nu = 800$ instead of 826). RAMAGE gives ('Roy. Soc. Proc.,' 70, 1901) 2780, 2718, in place of E. and H.'s 2780·28, 2719·76. It might appear, therefore, that 2718 is really a distinct line which, with the former, gives $\nu = 823·65$ (within errors of 826), whilst 2719·28 is the first of another doublet with $\nu = 826·68$. He gave also 2943·77, 2874·35 for D in correspondence with RYDBERG'S supposed 2966 and 2894. In the foregoing paper I adopted the same allocation for S (1, 2), and with it have taken E. and H.'s spark line 2481 as S_1 (3). For this it may be said that the corresponding lines come well in order as lying between the corresponding ones of Al and In, and the resulting formulæ constants also fit in well as between those of Al and In. On the other hand, they do not occur in the arc spectrum, where they ought to be stronger. Moreover, in E. and H.'s list, lines occur with the proper doublet separation and of corresponding nature and order of intensity, which certainly look as if they belong to the series; but, unfortunately, there are not sufficient to settle the question. The lines in question are given in wave-numbers as follows:—

D SERIES.

$m = 1$	(5r) 33954·36	**826·07**	(10r) 34780·43
	6·00		
	(10r) 33960·35		
$m = 2$	(39975·17)	**(826·00)**	(2r) 40801·17
	(2r) 39983·85		

[39975, suggested for D_{12} (2), has not been observed.]

S SERIES.

$m = 1$	(30r) 23961·41	**826·00**	(30r) 24787·44 (in both arrangements).
$m = 2$	(3) 36757·27	**826·68**	(2) 37583·95.

As against this allocation is the fact that they do not lie in corresponding positions between Al and In, as is seen at once from the values for the first two lines of the S_1 series, which are as follows :—

	Al.		Ga.		In.
S	3961	**211**	4172	**339**	4511
	2660	**59**	2719	**213**	2932

(The other allocation 2780 gives differences 120 and 152 for the second line, in closer ratio to those of the first.)

D	3092	2943	3258
	2575	2500	2714

They apparently belong to series of S and D type correlated to the typical ones. The limit is in the neighbourhood of 47600. If the real one is $47600+\xi$, the formulæ obtained for them give the following denominators, viz. :—

$$\text{For S } 1{\cdot}206859-{\cdot}0002477\xi-({\cdot}052878-{\cdot}0002022\xi)m^{-1},$$
$$\text{D } {\cdot}713106-{\cdot}0005393\xi+({\cdot}245010+{\cdot}0008706\xi)m^{-1},$$

and ξ may be as large as ± 250.

In the InS RYDBERG allocated the three first doublets and the first of the next. KAYSER and RUNGE brought the observed up to six, and the second lines of the next two $S_2(7, 8)$. This is curious, as the only example so far observed in which the second series appears stronger than the first. I find, however, that lines observed in the spark spectrum by HARTLEY and ADENEY ('Roy. Soc. Trans.,' 1884), viz., 2332·2 and 2191·2, occupy the places for $S_1(7)$ and $S_2(9)$. The other measures are K. and R.'s. Their value for 2357·7 is, however, clearly 1 A.U. too small. It gives an incorrect value for ν which the formula corrects.

In TlS RYDBERG gave the first four doublets and the five succeeding lines for TlS_2, indicating a similar result to that of In, viz., that the S_2 series are more persistent than the S_1. KAYSER and RUNGE extended the list by adding nine lines to the S_1 series, thus completing nine doublets and adding four extra lines to S_1. It is possible that even here the S_2 may be the more persistent, and that they have not been observed because they are situated much farther down in the ultra violet. The TlP series again are due to PASCHEN. The line $\lambda = 4678{\cdot}3$ is really a mean position for the doublet $TlP_{12}(7)$, the components being too close for resolution.

[*May* 13, 1912.—Whilst the foregoing has been passing through the press more complete lists of spectral lines, including those in the visible region, have been published by EXNER and HASCHEK.* It is possible, therefore, to see how far the

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* 'Die Spektren der Elemente bei normalen Druck,' FRANZ DEUTICKE, Leipzig u. Wien, 1911.

extrapolation in the text for the sharp series of Europium is justified. The suggested values for the lines were 5379·1 and 4711·69, with a probability that they should be about 2 A.U. higher, if the ratio $(\alpha+\Delta_2)/(\mu+\Delta_2)$ were to have the normal value ·2152. In E. and H.'s lists are found two doublets, 5381·46, 4713·77 ($\nu_1 = 2631{\cdot}39$) and 5377·13, 4709·95 ($\nu_1 = 2633{\cdot}63$). The former is the more probable as it gives the typical ratio α/μ more closely. The formulæ constants calculated from this are

$$40363{\cdot}19 - N/\{m+1{\cdot}292265-{\cdot}048561m^{-1}\}^2,$$

giving $(\alpha+\Delta_2)/(\mu+\Delta_2) = {\cdot}21636$ in place of the former value ·21246, and, therefore, closer to the value as given by other elements. The alteration in the constants is so slight that other measures, as, for instance, the estimated density of Eu, are not affected.

The supposed satellite series to EuS is not confirmed. At least there is no observed line with a wave-number near 18516·60. In the long series given at the bottom of p. 61, the first lines for S_1 and S_2 were extrapolated to wave-numbers 18858, &c. The nearest triplet to this is 5291·48, 4644·44, 4438·12, with wave-numbers equal to 18893·12, 21525·20, 22525·87, giving $\nu_1 = 2632{\cdot}08$, $\nu_2 = 1000{\cdot}67$. It fits in well as the first line of the series there indicated.]