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A Critical Study of Spectral Series. Part I: The Alkalies H and He

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III. *A Critical Study of Spectral Series.—Part I. The Alkalies* H *and* He.

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Notation and Abbreviations.

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

Adopted formula, $n = A - N\Big/\left(m+\mu+\dfrac{\alpha}{m}\right)^2$.

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

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

P denotes a principal series.
NaP the two principal series of Na.
NaP_1 is the first principal series of Na.
NaP_1 (2) is the second line in, &c.
CsD_{12} (4) denotes the satellite to the fourth line in the first diffuse series of Cs.

$m+\mu+\dfrac{\alpha}{\mu}$ is referred to as D except when there may be an ambiguity with diffuse, when den. is used.

$\dfrac{N}{D^2}$ is written V (*i.e.*, variable part of series). Thus—

VP (1) stands for the value of N/D^2 in P (1).

F is the symbol for the new series (fundamental) as P.S.D. stand for those already known.

f by itself stands for a fraction.

In referring to observers—

K.R.	stands for	Kayser & Runge.
L. & D.	,,	Liveing & Dewar.
B.	,,	Bergmann.
K.H.	,,	Konen & Hagenbach.
L.	,,	Lehmann.
Le.	,,	Lenard.
P.	,,	Paschen.
R.	,,	Ramage.
S.	,,	Saunders.
W.	,,	Wood.

The following investigation was commenced some years ago, at a time when the discussion as to the atomic weight of Radium raised the question as to the dependence on their atomic weights of the wave-lengths of corresponding spectral lines of different elements of the same group. The arguments were necessarily vague and unconvincing in the absence of any exact knowledge as to the connection of wave-length with atomic weight, even supposing such connection existed.

Our knowledge of series spectra is chiefly—one might say almost wholly—due to the sets of very exact measurements of KAYSER and RUNGE, and of RUNGE and PASCHEN, supplemented by extensions to longer and shorter wave-lengths by BERGMANN, KONEN and HAGENBACH, LEHMANN, RAMAGE, and SAUNDERS. These have been only quite recently added to by PASCHEN* and by the remarkable extension of the Sodium Principal series up to 48 terms by WOOD.† A most valuable feature of KAYSER's work was the publication of possible errors of observation. This has rendered it possible to test with certainty whether any relation suggesting itself is true within limits of observational error or not. In fact, without this, the investigation, of which the present communication forms a first part, could not have been carried out. So far as the author knows, SAUNDERS is the only other observer who has accompanied his observations with estimates of this kind. Others have given probable errors—practically estimates of the exactness with which they can repeat readings of that feature of a line which they take to be the centre—an estimate of little value for the present purpose. In deducing data from a set of lines it is thus possible to express their errors in terms of the original errors in the observations, and limits to the latter give limiting variations to the former. We therefore know with certainty what latitude in inferences is permissible, and are often enabled to say that such inference is not justifiable.

The formulæ of RYDBERG or of KAYSER and RUNGE are sufficient in general to identify lines as belonging to a given series, except in the cases of lines in the infra red, where the order is 1 or even 2, but they are not sufficiently accurate for our purpose. It is necessary to obtain formulæ for the various series which can reproduce the known series within limits of error or, if this is impossible, with as few outside as possible. The fact that RYDBERG's formula contains two arbitrary constants, whereas K.R.'s have three, and the well-known relationships brought to light by RYDBERG's formula naturally suggest it as the basis for a second approximation. In the absence of any definite theory as to the nature of the vibrations giving rise to spectral lines, it is necessary to make some assumption and to test it by its results. The most natural one clearly is to suppose that in RYDBERG's form $A-N/(D)^2$ where $D = m+\mu$, D is some function of m which can be expanded in a series of which $m+\mu$ is the first term. Comparison with observation shows that his formula becomes more exact with increasing m, and that, therefore, the function should be expansible in negative powers of m. In other words,

$$D = m+\mu+\frac{\alpha}{m}+\frac{\beta}{m^2}+\ldots,$$

where α, β are small.

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* 'Ann. d. Phys.,' 27, p. 537.

† 'Astro. Jour.,' xxix., p. 97.

If RYDBERG'S opinion, that the true formula should be of the form $f(m+\mu)$, is correct, then D would be of the form

$$D = m+\mu+\frac{\alpha}{m+\mu}+\ldots.$$

This, however, would be included in the previous formula with sufficient exactness except possibly for $m = 1$ or 2. Any term added to $m+\mu$ will, of course, by giving an additional arbitrary constant, produce a formula capable of reproducing spectral series with greater accuracy. The criteria justifying the form of a new term should be a very considerable increase of accuracy over a wide range (and particularly for $m = 1$), and that it should bring to light further relationships. RITZ,* from certain theoretical ideas, has taken $D = m+\mu+\beta/m^2$ or $m+\mu+\beta/(m+\cdot 5)^2$, and with a large number of series has obtained very close agreement. It was not until I had made some progress with this work that I became acquainted with his paper. I believe this to have been fortunate, for had I known his work, and the great increase of accuracy obtained by his forms, I should probably not have attempted to essay any further improvement. As it was I had proceeded so far as to feel certain that I was on correct lines, and had already obtained even more accurate results than his, besides some of the relationships presented below. The first important result was that it was rarely necessary to go beyond the α/m term—in fact, not at all for the alkali metals—that if α, β were both included, and, of course, an additional line used for calculation, β always came out a small fraction of α, and that with α alone the agreement was much better than with β alone (RITZ). Evidence of this is given below.

As will be seen later, there are indications that a form $D = m+\mu+\alpha/(m+\alpha)$ may be the true form, at least for certain series. These indications will be mentioned in due course, but as the metals of Group II. are not discussed in the present communication, the case may be further illustrated from a special series in Mg, which will at the same time serve to show that too much stress must not be laid in favour of a particular formula on the mere fact that it reproduces the observed lines, unless the observations are very exact, or comprise the first members and a considerable number of the others. The series in question was first discovered by RYDBERG† in K.R.'s observations, and consists of six observed lines contained between 5528 and 3987, which he called a "new kind of series" of the Mg spectrum. Neither his own nor K.R.'s formula reproduce the lines, and he suggested a combination of the two, viz.,

$$n = a-b/(m+\mu)^2-c/(m+\mu)^4.$$

As will be seen, this involves four constants and requires four lines to find the constants. The formula reproduces the two last lines within error of observation.

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[*] 'Ann. d. Phys.,' 12, p. 264.

[†] 'Ann. d. Phys.,' 50, p. 625.

To anyone using the form α/m, RYDBERG's new formula suggests at once the form $\mathrm{D} = m+\mu+\alpha/(m+\mu)$, which only requires three constants. Using the first three lines for these there results

$$n = 26617{\cdot}09 - \mathrm{N}\Big/\left(m + {\cdot}317620 + \frac{{\cdot}886213}{m+{\cdot}31762}\right),$$

which reproduces the last three lines well within the limits, as the table below shows. I felt no doubt but that this was the true form, until it occurred to me to test the simpler form.

The formula

$$n = 26609{\cdot}74 - \mathrm{N}\Big/\left(m + {\cdot}345117 + \frac{{\cdot}723502}{m}\right)^2$$

reproduces the last three quite as well as the other, and, in addition, possesses all the criteria of a diffuse series. The series is not, therefore, a "new kind of series," as it was called by its discoverer.

The following table gives the series with the excess of calculated over observed wave-length for each formula, and the limits of observational error :—

m.	λ.	Observational error.	RYDBERG.	$\alpha/(m+\mu)$.	α/m.
3	5528·75	·10	*	*	*
4	4703·33	·05	*	*	*
5	4352·18	·05	*	*	*
6	4167·81	·10	*	− ·08	+ ·09
7	4058·45	1·00	− ·20	− ·31	+ ·04
8	3987·08	1·00	+ ·48	+ ·39	+ ·89

* Used to calculate constants.

An interesting remark may be made here. If a series is represented by $\mathrm{D} = m+\mu+\alpha/(m+\mu)$ a slight alteration will represent it equally well by putting D a continued fraction, viz.,

$$\mathrm{D} = m+\mu+\cfrac{\alpha}{m+\mu+\cfrac{\alpha}{m+\mu+\ldots}},$$

in other words,

$$\frac{\mathrm{N}}{\mathrm{D}^2} \equiv \frac{\mathrm{N}}{\alpha^2}\left[\sqrt{\left\{\left(\frac{m+\mu}{2}\right)^2+\alpha\right\}} - \frac{m+\mu}{2}\right]^2$$

or

$$n = \mathrm{A} - \mathrm{B}\{\sqrt{(m^2+2am+b)} - (m+a)\}^2,$$

which looks quite different, and points to the frequencies depending on the roots of a quadratic.

In RYDBERG's formula the value of m (or μ) has a certain indeterminateness—μ

may be a positive or negative fraction, or may be > 1. If we know that the first observed line of a series is actually the first member, $m = 1$ for that line and μ is definite. If we assume, for instance, that the first doublet of a principal series has the same separation as those of the associated series, the question is settled; or if such a line has not been observed, then the degree of convergence of the separation of any P doublet will give its order at once, *e.g.*, the fact that the D lines in Na have the same separation 17·21 as the sharp series, would show that the D lines are actually the first members of the series. If these had happened to have been outside the region of observation, however, and the doublet (3302, 3303) had been the first observed lines of the P series, their separation (5·50) would have at once shown that for them $m = 2$, and again μ would be definitely determined. In spectra with no doublets or triplets, as in the singlet series of He or O, this criterion would not be available. Recourse might then be had to the fact that in all known cases the first line of a P series is not very different from the first line calculated from any approximate formula of the sharp series with sign reversed. It was this consideration which led RYDBERG to postulate a value for $\mu > 1$ in the principal series of the alkali metals. In all cases there is nothing to distinguish the order for a diffuse series. If, therefore, we wish to discuss how the value of μ changes from element to element, RYDBERG'S formula can only give an approximation to its fractional part alone. As soon, however, as a more approximate formula, such as that used in this paper (α/m) or that used by RITZ (α/m^2), is applied, μ becomes definite at once—*e.g.*, in the principal series of the alkalies the denominator is (f denoting a fraction) $m+1+f-\alpha/m$ and not $m+f-\alpha/m$, for the latter will not reproduce the series within the limits of observational error, and consequently $\mu > 1$; in the sharp series $\mu < 1$. In the sharp series, however, of Group II. or the Zn group $\mu > 1$, from which it may be remarked incidentally it follows, using RYDBERG'S law, that the wanting principal series must be looked for in the ultra-red. The unique determination of μ is a matter of the first importance for comparative study. It only fails when the lines are so few or the measurements so bad that α/m or $\alpha/(m+1)$ will either of them reproduce them within the observational limits.

In order to draw safe conclusions as to any relationships between the constants for various elements, or between the different series of the same element, we need to know their limits of possible variation. This is possible, as mentioned above, when the data are based on the measurements of KAYSER and RUNGE or of SAUNDERS. It is not proposed, in what follows, to give complete expressions for these variations in terms of observational errors, but the method can, perhaps, be understood best by taking an actual example—say that of K.S. The wave-numbers of K.S. (3.4.5) reduced to vacuum from the wave-lengths given by K.R. are 14407·80, 17230·72, 18721·20, with possible errors, as deduced from wave-length errors of 1·04, ·15, ·53 respectively. The true values are taken to be $14407·80+1·04p$, $17230·72+·15q$, $18721·20+·53r$, where p, q, r may have any values from -1 to $+1$. The lines as observed give $A = 21963{\cdot}38$, $\mu = {\cdot}825786$, $\alpha = -{\cdot}047604$. The variations due to the errors are found to be

$$\begin{aligned} \delta A &= -{\cdot}673p + {\cdot}520q - 1{\cdot}988r, \\ \delta\mu &= {\cdot}001646p - {\cdot}000969q + {\cdot}002540r, \\ \delta\alpha &= -{\cdot}005216p + {\cdot}002514q - {\cdot}006116r. \end{aligned}$$

If, then, the constants calculated from three observed lines give a formula which brings a particular line outside the limits, it is possible to determine whether a permissible change in the original wave-lengths can bring it within. It is used also to test the validity of RYDBERG'S law as to the limits of S. and P. A further valuable result is that it enables us to give the limits of possible variation of A, μ, α, *e.g.*, in the example above cited by putting $p = -q = r = \pm 1$. The utmost possible, though unlikely, variations are then $\pm 3{\cdot}18$ for A, $\mp {\cdot}005155$ for μ, and $\pm {\cdot}013846$ for α. When in the following pages limits of this kind are given, it will be understood that they have been arrived at in the above manner.

We shall have to apply certain laws and relationships already known, and it is necessary to have some clear idea of the degree of exactness with which they represent facts. Some of these depend on direct observation, others on relationships arising from the formulæ. Of the former the most important relate to the doublet (ν) and triplet (ν_1, ν_2) separations of the various series. They are :—

(A) The value of ν (or of ν_1, ν_2) is the same for all the members of either the sharp or diffuse series—the separation in the diffuse series being taken between the satellite of the first and the second, and in the case of triplets for ν_2 between the satellite of the second and the third.

(B) The values of ν for sharp and diffuse are the same.

(C) The value of ν for the first line of the principal series is the same as for the sharp or diffuse.

It may be said at once that these statements are true within the limits of observational errors, the only exceptions that I have met with are in the case of the sharp series of oxygen and the diffuse of sodium. O.S (4) gives ν as lying between 3·52 and 3·72, and O.S (5) as between 2·82 and 3·46, or say $\nu > 3{\cdot}52$ by the former and $< 3{\cdot}46$ by the latter. One is naturally tempted to put this down to a larger observational error than the estimated one. There are cases, however, in which a doubt may arise as to whether these statements are absolutely exact. For instance, NaD gives the following values for ν (the observational errors are given in brackets) :—D (3) 16·60 (·5); D (4) 17·04 (·8); D (5) 19·28 (2·3); D (6) 28·18 (5). It is to be noticed the least possible ν from D (6) is 18·18, and the greatest from D (3) is 17·60. If it is real, (A), (B) are not true, but D_1 (6) and D_2 (6) are bad measurements, and the limit of accuracy (5) given for each is probably a rough way of saying very large. On the other hand the gradual rise with increasing order raises a suspicion that the rise exists and that ν is not constant. It is just possible, as we shall see later, that the sodium series, which has generally been taken as the typical diffuse, may not be so.

As regards (B), the following table gives the values of ν for the alkalies, as determined by least squares (duly weighted) for Na and K and arithmetical means for Rb and Cs from the observations of K.R., SAUNDERS, and RAMAGE :—

	Na.	K.	Rb.	Cs.
Sharp	17·10	57·67	237·39	553·89
Diffuse	16·89	58·02	236·30	551·30
Both	17·07	57·84	236·78	552·22

Any doubt, however, as to the exact truth of (A) and (B) must vanish when we consider those elements in which ν is very large. As examples, take Tl for doublets and Hg for triplets. In the case of Tl we find the following values of ν :—

Sharp.	Diffuse.
7792·37 (·31)	7793·08 (·63)
7792·63 (·73)	7792·64 (·87)
7792·46 (1·18)	7791·69 (2·40)
7790·92 (2·75)	7791·68 (6·82)
7789·22 (7·22)	7790·22 (8·14)
Most probable ν = 7792·39.	Most probable ν = 7792·90.

Most probable supposing both same = 7792·51.

The corresponding values for Hg are :—

	Sharp.	Diffuse.
ν_1	4631·78	4631·79
ν_2	1767·59	1768·52

If there were real variations, we cannot but believe that they would bear some relation to the absolute magnitude of ν. Yet here, even with such exceedingly large values of ν, the variations do not exceed the corresponding values for small ν. We need, therefore, feel no hesitation in imposing the laws (A) and (B) as conditions which our formulæ must fulfil.

As to (C) there cannot be quite the same degree of certainty. The principal series have only been observed in the alkali metals and He among doublets and O and S amongst the triplets. In the alkali metals ν for NaP (1) is known with extreme accuracy, viz., $\nu = 17·21$ (from interferential measurements). For the others the measurements are very bad. For K, KAYSER and RUNGE give 57·08 (very large possible errors), SAUNDERS 57·87, and LEHMANN 56·43. For Rb, SAUNDERS gives 237·73, LEHMANN 232·76. For Cs, LEHMANN gives 553·00. In every case (C) is true within limits of errors of the measurements, but those limits are very wide, and it may well be that exact equality does not hold. There can be little doubt but that the value of ν from NaS is very close to 17·10, and 17·21 is certainly exact for NaP (1). The He lines have been measured with great exactness, but unfortunately ν is small (1·007) and HeP$''$(1) is far up in the ultra-red. In O, ν is of the order 3·6, and OP (1) is a bad observation, whilst in S ($\nu = 18·04$), SP (1) is outside the region of observed lines. The evidence of the exactness of (C) is, therefore, not conclusive, but in spite of the indications of Na to the contrary, it is probably correct. The doubt, however, should be kept in remembrance.*

Observation also tends to show that :—

(D) The corresponding S and D series tend to the same limits.
(E) The doublet or triplet series of the P type tend to the same limit.

The exact truth of (D) and (E) has not been proved from direct observation, for the actual limits have never been seen nor have a sufficiently high order of terms been observed. The HD has been measured up to $m = 31$, but HS (star by PICKERING) only a few to compare with it. NaP_1 has been measured by WOOD† up to $m = 43$ as an absorption spectrum, but only two terms of NaP_2 are known. With the exception of these two, no series has yet been observed nearly up to its limits, and the strongest evidence in favour of (D) and (E) is based on the limits as calculated from formulæ—in which again the actual limits will vary slightly with the form adopted for the formula.

The lists of values of limits given by RYDBERG‡ show that the approximate truth of (D) is certain.

Amongst the relationships depending on the formulæ, the chief are those which will always be associated with the name of RYDBERG, viz., the remarkable connection between the sharp and principal series, and the constancy of N. The former may be expressed in the form :—

(F) $S(\infty) = N/D^2$ of $P(1) = VP(1)$§.
(G) $P(\infty) = N/D^2$ of $S(1) = VS(1)$.

The discussion of the evidence for or against them will come later. Their approximate truth is so clear that it would require very strong evidence to justify the use of any formula which did not conform to it. RITZ has imposed the law on his formula, using it in calculating the constants, and supposes that the results prove

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* Since the above was written, PASCHEN has published further observations in the ultra-red, giving what he takes to be the principal series for several elements. When discussed, these will probably give considerably more light on the question. 'Ann. d. Phys.,' vol. 29, p. 625.

† 'Astro. Jour.,' vol. xxix., p. 97.

‡ 'Rapports Congrès Internat. de Phys.' II., p. 210.

§ The expression "N/D^2 of" will have to be employed so frequently that it will be convenient to use a symbol for it. V will stand for the term of the formula in which m varies.

its truth. When, however, his values are contrasted with actual measurements (see below), it would appear rather to show that if the law is correct his formula is wrong, or if his formula is correct the law is not exact.

(H) The value of N is the same for all series and for all elements.

There can be little doubt but that N is very nearly the same for all known series, and it is a tempting hypothesis that it is actually so. We have no evidence, however, to prove that it is either the same for all series, or has different values for the different types of series, which may well be the case. If it be found that all observed lines come into the formula with the same value of N, and *further* if thereby the validity of (F) and (G) can be established, or if other relationships which present themselves are more clearly brought out, then the evidence that N is a constant of nature (as RYDBERG calls it) will be very strong. We shall start, therefore, by taking N to be the same for all series, and the same which RYDBERG assigns to it, viz., 109675, when referred to vacuum.

This value, however, may require redetermination. It was determined by RYDBERG from hydrogen by least squares applied to BALMER'S formula for HD and using the observations of AMES. It was BALMER'S form which led to RYDBERG'S modification, putting $m+\mu$ in place of m, where μ depends in some way on the properties of the substance. To suppose, therefore, that BALMER'S formula is exact, *i.e.*, $\mu = 0$, seems like saying that hydrogen has no individual properties. In any case, it would seem extremely unlikely that, as every other substance has a finite value of μ, H should have $\mu = 0$. It is to be expected that its μ would be small. All the low atomic weight elements have μ small (or very nearly unity) for a D series, and we should expect the lightest element of all to have a very small one (or nearly $= 1$). To find N, then, the series of RYDBERG should be used as a basis, and N and μ both determined. Unfortunately the HD spectrum is not known with great exactness of measurement. The most accurately measured spectra as wholes are without doubt those of He by RUNGE and PASCHEN, and it would seem preferable to use these to determine N. At first sight, then, it might appear more logical to consider this point of the value of N as determined from H and He spectra before going further. It is preferable, however, to postpone this until the alkali spectra have been discussed, and some information obtained as to the connection of the different types of series. Moreover, by keeping at present to RYDBERG'S value, it will be possible to directly compare the results from the formula adopted in this paper with those from that of RITZ, which is the only other comparable in accuracy.

The Spectra of the Alkali Metals.

As SAUNDERS has given very complete tables of the observed spectra of the alkalies,[*] it will be sufficient to refer to them for the material at disposal at that date.

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[*] 'Astro. Jour.,' xx., p. 188.

Since then we have had the very exact measurements by Paschen* in the ultra-red of Li, Na, and K, and the remarkable discovery by Wood† of the absorption by its own vapour of the NaP series, lines being observed down to $m = 48$.

A superficial examination of the series of the different alkali elements shows that Li apparently occupies an anomalous position, and leads to the surmise that the series are not homologous with those of the other elements. Thus, if the first lines of the principal series in each be compared, viz.,

Li.	Na.	K.	Rb.	Cs.
6708	5890	7665	7805	8527

it is seen that the wave-lengths continually decrease with decreasing atomic weight until we arrive at Li, when the wave-length jumps back above Na. Further from analogy with the others LiP (1) should be a doublet with $\nu = 1 \cdot 5$ about, and the LiS and LiD should be all doublets of the same ν, but, as a fact, they are all single, with the possible exception of 4602, which Konen and Hagenbach believe to be a double line. For this reason in my first examination I left Li for separate consideration, and as this was fully justified by the result, it may be well to proceed on the same lines now. We shall discuss then first the well-known principal, sharp, and diffuse series of the other alkalies, then the additional series which appear in the spectra, and finally return to Li in the light of knowledge gained from the others.

The first step is to justify the use of the form $m+\mu+\alpha/m$ for the denominator, by showing how closely it reproduces the observed lines. This is done in Table I. For comparison the results as calculated from Ritz' formula are also given. In each series the first column (O) gives the possible observational error, the second (H) the excess of observed over the calculated wave-length, and the third (R) the corresponding values from Ritz' formula. Whenever this is outside the observational error it is printed in thick figures. For the present purpose the values for Li are added. The values of μ, α, &c., are given in Table II. The results for Ritz are given from his paper, or, for those lines not observed at the time, are calculated from his constants. It should be remembered that the estimated possible errors are considerably greater than the probable errors, and consequently we ought to look for a closer agreement between calculated and observed values than the possible errors show. It should further be noted that for high orders any formula giving rough approximation only will give some information as to the excellence or otherwise of the observations themselves. If the deviations show gradual change as m increases, the formula is probably in fault; if, however, a deviation makes a sudden change and comes back to its former course as m increases, the observations are probably the cause.

Where two values are given under P they refer to the doublets. All the S have

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* 'Ann. d. Phys.,' 27, p. 567.

† 'Astro. Jour.,' xxix., p. 97.

TABLE I.

Principal series.

m.	Li.			Na.			K.			Rb.			Cs.		
	O.	H.	R.	O.	H.	R.	O.	H.	R.	O.	H.	R.	O.	H.	R.
1	·2	0	0		0	0	5	− 4	0	?	0	0	?	0	0
					0	0		− 4·6	− ·24		− 2·5	3·5			
2	·03	0	0	·03	0	**·03**	·03	0	0	·03	0	0	·05	− ·02	0
					0	0		0	0		0	0		·04	− **·07**
3	·03	0	**·07**	·05	0	− **·10**	·03	0	**·13**	·05	0	0	·10	·42	0
								0	**·12**		0	·02			− ·04
4	·03	**·06**	0	·1	·03	− ·08	·03	0	0	·05	0	− **·11**	·20	− ·09	− **·72**
								·02	− **·05**		**·06**	0	·30	− ·22	− ·14
5	·1	− **·16**	**·20**	·1	·02	− **·13**	·10	**·21**	·10	?	·02	− ·55		− ·05	0
								·18	− **·40**		− ·04	− ·62			
6	·1	− **·12**	·01	·1	− ·09	− **2·2**	·10	0	− **·20**	?	1	·38		− ·14	− ·15
											·27	− **·33**			
7	·2	− ·07	·03	·2	− ·01	− ·15	·15	·01	− **·19**					·67	·41
8	?	+ ·08	·10	*	− ·13	− ·25	·20	− ·06	− ·13					·30	·02
9	?	·21	·22		− ·07	− ·19	1·00	− ·09	− ·27					− 2·1	− 2·4
10					·01	− ·10									
15					− ·05	− ·16									
20					− ·10	− ·21									
25					− ·09	− ·21									
30					− ·17	− ·28									
35					− ·10	− ·22									
40					− ·09	− ·20									
45					− ·07	− ·19									
48					− ·16	− ·27									

* WOOD'S values.

TABLE I. (continued).

Sharp series.

m.	Li.			Na.			K.			Rb.			Cs.		
	O.	H.	R.	O.	H.	R.	O.	H.	R.	O.	H.	R.	O.	H.	R.
2		0 P.	·75 L.	1·0	**1·37**	**1·05**	1·0	**16·20**	**1·11**	?	26 B.	– 17		104	
3	·10	0	0	·1	0	0	·5	0	0		·12 S.	0		0	
4	·20	0	– ·08	·1	0	– **·25**	·05	0	**·20**	·2	0	**1·8**		0	
5	·20	·06	– ·04	·15	0	– **·23**	·15	0	**·22**	·15	0	**1·6**		0	
6	3	2·3	2·1	·2	**·42**	**·21**	·20	·01	**·22**		0	1·56 S.		·17	
7				?	– ·12	– ·17	1·0	·17	**1·10**		– ·09 R.	·09 S.		·24	
8				?	– ·32	– ·44	L.D.	– ·22	·25		·25 S.	·40 R.			
9							R.	·67	1·18						
10															

Diffuse series.

m.	Li.			Na.			K.			Rb I.			Rb II.			Cs.		
	O.	H.	R.	O.	H.	R.	O.	H.	R.	O.	H.	R.	O.	H.	R.	O.	H.	R.
2	·03	0		·30	0		·5	·38		?	319			278				
3	·1	0		·15	0		?	1·1		·9 ?	– ·51			0		L.	– 4·90 – 3·19	
4	·2	0		·2	0		·05	0	0	·2	·04			0		S.	0	
5	·2	– ·18		·5	– ·20		·15	– ·11	0	·15	– ·01			0		S.	0	
6	5	– ·31		1	**1·11**		·2	·14	·15	·15	·01			0		R.	0	
7	5	– 1·65		?	– ·97		1·0	·40	·7	R.S.	·25			·16		R.	·01 0	
8	5	– 1·35		?	1·57		L.D.	1	14·5	S.	·50			·43		R.	·17 ·05	
9							L.D.	– ·26	12·6	S.	·41			·34		R.	·55 ·22	
10										B.B.	·09			·02		R.	·41 2·08	
11										R.	1·25			·91		R.	– ·01 1·15	
12										K.H.	1·25			1·17				
					$\mu = 1+f$.			$\mu = f$.			$\mu = 1+f$ and S's value of D_{11}.			$\mu = 1+f$ and no satellite.				

been found by correcting to constant ν, also in P_2, $P_2(\infty)$ has been taken to be the same as $P_1(\infty)$.

Remarks on Table I.—NaP. It will be seen that agreement is perfect in NaP. This is the only series in which the first three lines (from which the constants are determined) are known with great accuracy. It has not been thought necessary to give the comparison with all Wood's measurements, but after $m = 10$ they are given for every interval of 5. The deviations from Wood show that his observational work (apart from instrumental) have mean errors of about ±·05 A.U., and if his instrument constants are comparable with K.R.'s, the constant $P(\infty)$ in the formula should be about ·10 higher. Ritz has two outside, one 1·3 times and the other more than twice the amount allowable.

NaS is not a first-class set of measurements. Nevertheless, there is good agreement except for S (6). For S (2) Paschen's estimate of possible error is 1. For this a very slight alteration in the value of α, or an error of ·01 in S (3) (possible error = ·10), would bring both mine and Ritz' values within limits of error. The deviation in S (6), however, is serious. It has the appearance of being chiefly due to a measurement error, for successive deviations, as m increases from 4 to 8, are 0, 0, +·42, −·12, −·32, and Ritz' formula suggests the same. If the observations are looked at more closely S (6) gives $\nu = 15·89$ instead of 17·2. Liveing and Dewar, in their early measurements of this doublet, say: "The lines 4543·9, 4540·2 in the Normal Solar spectrum probably represent this pair." These give $\nu = 17·94$. L. and D.'s measurements are, of course, not to be compared with those of the later observers, but apparently their method of producing the light had advantages over those of K.R. Their observations generally give wave-lengths less than those of K.R., but in this case they are much less, pointing to a suspicion that instead of $\lambda = 4546·03$ one nearer 4544·8 would be more correct. $\lambda = 4545·61$ is that demanded by the formula. Although, therefore, this case is a serious one against both formulæ, there are yet indications that it may be closer to the real value than the observations show. S (7.8) are from L. and D.'s observations. The reading for S (8) is given by them for the middle of a narrow band which they have not seen divided. For this $n = 23015·49$. I have taken the readings for the two lines to be $23015·47 \pm \frac{1}{2}(17·2)$, and Ritz' result is also compared with this.

NaD. The observation errors for all the NaD series are large. The deviation from constant ν has been referred to already, especially the excessive ν of D (6), which renders the readings for this very doubtful. The constants have been determined from L.'s readings for D (2) and K.R.'s for D (3.4). There is some uncertainty as to whether μ for the D series should be a fraction or 1+fraction. The results here are calculated for the form 1+f, but in all cases for D lines in this table the order of a line is taken to be the integral part of the denominator whether we use $\mu = f$ or 1+f. The doublet at $m = 6$ is outside the limits, and it ought to be if ν is to be constant, also the reading for $D_2(5)$, but both $D_2(5)$ and $D_2(6)$ can be brought within by a permissible change in $D_2(2.3)$, thus leaving $D_1(6)$ outside, which must necessarily be the case with ν so large as 28. We may regard, therefore, the formula as satisfying the conditions for NaD. RITZ gives no constants for his formula for this series.

KP. The observations for P(1) are very bad. K.R. give 7665·6 and 7699·3 (possible errors 5). L. gives 7668·54 and 7701·92, R. 7664, and S. 7664·91 and 7699·08. HERMANN* 7665·29, 7699·32. The votes carry it for the lower value of P, and one gets an almost superstitious belief in K.R.'s measurements after long use of them in this kind of work. On the contrary, L.'s result appears to agree better with those computed from K.R.'s values of P (2.3.4), the case here adopted. RITZ' constants are calculated from L.'s result for P (1) and K.R.'s for P (2.3). In the table, then, L.'s result is used. It will be seen that the formula adopted here gives excellent agreement except in P (5), where the deviation is twice that allowable. The order from $m = 2$ to 7 is 0, 0, 0, ·21, 0, ·01, a striking agreement with a sudden jump at $m = 5$, pointing to observational error, but there is no further evidence as in the case of NaS (6). RITZ' are all outside, except for $m = 8$, 9.

The S are corrected to constant $\nu = 57{\cdot}93$. The agreement is very good except for S (2), which is far out. RITZ has all outside. In his paper he must have given $S_2(\infty)$ for $S_1(\infty)$. I have calculated his S (2.8.9) on this supposition.

The numbers for KD are calculated from a form $\mu = \mathrm{f}$. It appears $\mu = 1+\mathrm{f}$ is not possible. As is seen, there is good agreement. In this case, in order to bring D (2) within limits, errors have been allowed to D (3) and D (5). This is the only diffuse series for which RITZ has given constants, and I have calculated from them the values for $m = 2.3.8.9$. The formula in this case is quite out.

RbP. The only accurate measurements for this series are those of K.R. for P (2.3.4). P (1) is as uncertain as in the case of KP (1). K.R. give 7950, 7811 (observational error = 5) with $\nu = 223{\cdot}85$; at least one, therefore, is certainly wrong. L. gives 7950·46 and 7805·98 ($\nu = 232{\cdot}76$); S. gives 7947·6 and 7800·2 ($\nu = 237{\cdot}73$); whilst R. has 7799 for $P_1(1)$. Using $P_1(2.3.4)$ for constants gives $P_1(1)$ close to L.'s value and $P_1(5)$ close to observed value, pointing to L.'s value for P (1) as being very close to the truth and that K.R.'s error is almost wholly in $P_1(1)$. K.R. and L. agree practically for $P_2(1)$. S. gives a line at 3158·7 which is closer to $P_2(6)$ than $P_1(6)$; it has been taken for both lines in the table. For P_2 the limit has been made the same as for P_1, and the lines $P_2(2.3)$ used for calculation. $P_2(4)$ is just outside, but a slight permissible alteration will bring it inside.

RbS. The text for this series is very corrupt. K.R. only observed $S_1(4.5)$ and $S_2(4)$ with possible errors ·2 for $m = 4$ and ·15 for $m = 5$. For S (3) L.'s measurements give $\nu = 239{\cdot}62$ and S.'s 237·60. For the constants I have used S (4.5.6) corrected to $\nu = 236{\cdot}70$. The formula gives S.'s result for S (3) as against L.'s. S (7.8) are given both by R. and by S.: for lack of any other guidance I have taken

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* 'Ann. d. Phys.,' 16, p. 684.

that which agrees most closely with that calculated from the formula, and I have treated Ritz in the same way, calculating his S (2.6.7.8). The observations for S (2) are by B. They are in no way comparable with the corresponding values by P. in the case of Na and K. In fact, B.'s readings give $\nu = 245{\cdot}07$, or an error of about 16 A.U. in the wave-length differences of S_1 (2) and S_2 (2). Probably Ritz is closer to S (2) than the formula in α/m; on the other hand, he has errors from nine to ten times the allowable in two cases.

RbD. In the D series it has been thought that Rb has a satellite to 7753 (L.), viz., 7759 (S.). If we take $\mu = \mathrm{f}$ and use K.R.'s values for D (4.5.6), it can be shown that it is impossible to get within wide limits of either S. or L.'s D (3), or of Bergmann's D (2); but it is possible to satisfy conditions for D (3) if what has been supposed to be the satellite is actually the line D_{11} (3), *i.e.*, 7759·5 S. instead of 7753·58 L., but still D_1 (2) comes far wide of B.'s value on the side of longer W.L. With $\mu = 1 + \mathrm{f}$ the calculated place of D_{11} (3) is close to the supposed satellite, and it can only be modified to bring it to the supposed D_{11}, *i.e.*, 7753, by giving large possible errors, alternately positive and negative, to K.R.'s observations of D (4.5.6). Also the D_{11} (2) line, as calculated, falls half-way between B.'s D_1 (2) and D_2 (2). It can be made to fall on his D_2 (2), but not on his D_1 (2). I am inclined to think, first, that B. has a large error here, and, second, that Rb has no satellite series. There are two additional considerations pointing to the same conclusion. One is that, if a satellite series exist, the doublet separation for D (2) will be considerably less than the normal (237). Now B.'s two lines $n = 15410$, 14830 (those now taken to be D_1 and D_2) give 253·73, about 40 A.U. above the normal; whereas, if there were satellites, it should be expected to be somewhere about 40 A.U. less. Although B.'s actual wave-lengths in this region might possibly err to this amount, it is not probable that the difference of two lines so close should be wrong to the extent of 80 A.U. as they would be if satellites existed. The other reason against Rb having satellites is considered later in p. 86. The agreement of the formula with observation for the whole spectrum when no satellite is supposed is remarkable. The values are given for this case in the Column Rb II., and for the case of satellites in Column Rb I.

CsP. K.R. have only three lines, of which one alone is good. R. has given from P (2) to P (9); L. has given P (1) with $\nu = 553$. R. practically agrees with K.R. for P (2), but deviates in P (3) from them by four times their estimated possible error (·1). The observations of R. were made with the oxyhydrogen flame, and the spectra were probably better developed than in K.R.'s case. To compare the two, I have calculated out the doublets, taking $\nu = 553$ for the first. For this purpose any approximate formula will serve. The result is 553, 184, 84·2, 45·5. K.R.'s give 181·07, 80·2, 41·1, and R.'s 180·8, 82·5, 45·3, which favours R.'s values for P (3) and P (4). I have therefore calculated constants from R.'s P_1 (2.3) and L.'s P_1 (1), and those for P_2 from $P_2(\infty) = P_1(\infty)$, L.'s P_2 (1) and R.'s P_2 (2). In the table I have entered the deviations from K.R.'s values for (2.3.4). Really, therefore, for our formula the apparent deviations are the deviations between K.R. and R. I have entered them thus because K.R.'s observation errors are entered, and it would be misleading to enter 0 against them. It reproduces the whole of RAMAGE'S results very closely. RITZ calculated from L. and K.R. His difference for P_2 (2), though actually greater than the limit, is probably not due to the form of his formula, but to K.R.'s errors, and should not be counted.

CsS. Here S_2 (3) is by L., S (3–5) by S., and S (4–7) by R. The values of S (3.4.5) of SAUNDERS corrected to constant $\nu = 553$ were used to determine the constants. There are no estimated possible errors to compare with. S (2) by B. gives $\nu = 582·08$. If his readings share the error equally, then the difference between observed and calculated wave-length is 74. It is probable that this is chiefly due to imperfection in the formula. RITZ has given no formula for this series.

CsD. The D series differs in Cs from the other elements in the clear possession of satellites, and consequently there are two distinct series to find, D_{11} and D_{21} no longer differing by the same amount. The form $m = 1+f$ gives the best result. The tabulated numbers are those determined for the D_{11} and D_{21} series, as the D_{21} are always stronger lines than the D_{12}. The formula calculated from the D_{12} lines (the so-called satellites) differs only very slightly from that calculated from D_{21}. They should, of course, be the same (limits excepted). If the values of N/D^2 for $m = 1$ (the top line) be calculated from the two formulæ they are found to be respectively 17134·86 and 17140·64. They should be the same; their mean is 17137·75. The difference between VD_{11} (2) (17040·68) and this is 97·07. The significance will be seen when the additional series are discussed.

The table also contains the corresponding deviations for the Li spectrum, but the consideration of details is better postponed until that element is dealt with specially.

The following list of excessive deviations of the formula is excerpted from Table I. —only in place of the actual deviations the ratio of the deviation to the maximum allowable is given :—

H.	R.	H.	R.
	LiP (3) 2·3	KP$_1$ (5) 2	KP$_1$ (5) 1
LiP (4) 2		KP$_2$ (5) 1·8	KP$_2$ (5) 4
LiP (5) 1·6	LiP (5) 2		KP$_1$ (6) 2
LiP (6) 1·2			KP$_1$ (7) 1·2
	NaP$_1$ (2) 1	KS (2) 16	
	NaP$_1$ (3) 2		KS (4) 4
	NaP$_1$ (5) 1·3		KS (5) 1·5
	NaP$_1$ (6) 2·2		KS (6) 1·1
	NaS (4) 2·5		KS (7) 1·1
	NaS (5) 1·3		RbP$_1$ (4) 2
	KP$_1$ (3) 4		RbS (4) 9
	KP$_2$ (3) 4		RbS (5) 10
	KP$_2$ (4) 1·6		CsP$_1$ (4) 3·6

The case NaS (6) is not included, as there is strong evidence that the readings are not correct. There is some indication also of the same for KP (5). The formula is bad for the top line of the KS series, and this must be specially considered in the sequel. With this exception the agreement is remarkable.

Preliminary Discussion of Formulæ Constants.

Table II. gives the various constants determined under the conditions described above. The possible maximum variations are given in all cases where K.R. give possible errors of observations. Where these are given in brackets the numbers show how the last digits in the constant are affected. Thus in NaP $\mu = 1\cdot148678 \pm (477)$. This means that μ may differ from 1·148678 by any amount less than ·000477. It is to be understood that in any one formula the top and bottom signs go together. Thus if NaP (∞) be taken as $41446\cdot76 + 1\cdot69$, μ must be $1\cdot148678 - \cdot000477$, and so on. It should also be noted that the variations in P, μ, α are not necessarily proportional, *i.e.*, if the error in P (∞) is one-half of 1·69, the corresponding errors in μ, α

TABLE II.—Formulæ Constants.

	P.		
	P (∞).	μ.	α.
Na . . .	41446·76 ± 1·69 1·626740 ∓ (33)	1·148678 ∓ (477) 2·116902 ∓ (70)	– ·031776 ± (407)
		1·147878 ∓ (477) 2·116162 ∓ (70)	– ·031716 ± (407)
K. . . .	35006·21 ± 1·55 1·770032 ∓ (25)	1·296480 ∓ (1492) 2·233969 ± (1056)	– ·062511 ± (2548)
		1·293459 ∓ (1492) 2·231041 ± (1056)	– ·062418 ± (2548)
Rb . . .	1·20 33687·50 ± 2·09 32 1·804344 ∓ (53)	443 1·366399 ∓ (1140) 16 2·291845 ∓ (379)	427 – ·074554 ± (1519)
		1·353346 2·278964	– ·074382
Cs . . .	31400·16 ± $d\xi$ 1·868908 ∓ (297) $d\xi$	1·450967 2·360890	– ·090077
		1·419166	– ·090766

TABLE II.—Formulæ Constants (continued).

	S.		
	S (∞).	μ.	α.
Na . . .	24472·11 ± 3·84 2·116986 ∓ (165) ν = 17·11	·655793 ∓ (5368) 1·629512 ± (8357)	− ·026281 ± (13725)
K. . . .	21963·38 ± 3·18 2·234625 ∓ (161) ν = 57·87	·825786 ∓ (5155) 1·779182 ± (8691)	− ·047604 ± (13846)
Rb . . .	$20869\cdot73\,{}^{+4\cdot46}_{-3\cdot46}$ $2\cdot292426\,{}^{-(245)}_{+(190)}$ ν = 237·98	$\cdot876910\,{}^{-(9438)}_{+(5702)}$ $1\cdot815040\,{}^{+(16066)}_{-(3178)}$	$-\cdot061870\,{}^{+(25504)}_{-(8880)}$
Cs . . .	19671·48 ± ξ 2·361214 ∓ ·00006ξ ν = 553·96	·957661 1·885620	− ·072041

	D.			
	D (∞).	μ.	α.	
Na . . .	24467·09 ± 2·77 24471·68 ± 3·48 24484·70 ± 2·77	1·988393 ∓ (1566) ·984712 1·988038	·001638 ± (1206) ·009521 ·001740	} D_1. D_2.
K. . . .	$21971\cdot67\,{}^{-4\cdot85}_{+6\cdot64}$ 21963·33	$\cdot690743\,{}^{+(5100)}_{-(31446)}$ 1·713039	$\cdot306864\,{}^{-(17150)}_{+(103360)}$ ·168437	
Rb . . .	20876·45 ± 5·37 20874·81 ± 4·8 20874·37	·621384 ∓ (12409) $1\cdot636355\,{}^{-(9796)}_{+(13258)}$ 1·637432	·240186 ± (39684) $\cdot137577\,{}^{+(7513)}_{-(16111)}$ ·134888	} Satellite. No satellite.
Cs . . .	19673·31 19674·26	·529963 1·529196 ·521795	·013957 ·009481 ·009248	} D_{11}. D_{12}.

are not necessarily one-half of $-(477)$ and $+(407)$. The variations given are the greatest allowable subject to observational errors alone, and the assumed value for N, but that they should be so great as these must be regarded as highly improbable. The variations for KP are so large because the constants are determined from P (2.3.4) instead of P (1.2.3), a less accurate value of P (1) being more effective for correct determination of μ or α than a more accurate one of P (2). Two estimates are inserted for RbP (which were deduced from P (1.2.3)), the larger are based on K.R.'s estimates of possible error, the smaller on L.'s estimate of probable error; the truth probably lies between the two. Different positive and negative errors appear under RbS and KD. This is due to the fact that small permissible errors were introduced into the observations giving the constants in order to bring all the calculated series within limits. The values of ν inserted in the table give the values used in correcting the two sharp series to a constant ν. They are not the same as those given elsewhere as the most probable values, but as they were used in the original calculations, and as nothing was to be gained by recalculating, they are left as they were.

The first column under each series gives the value of the limit A; the top number being its value and the lower the value of the D when it is written in the form N/D^2. Thus in NaP

$$P(\infty) = 41446{\cdot}76 \pm 1{\cdot}69 = N/(1{\cdot}626740 \mp {\cdot}000033)^2.$$

The third line under P gives the values for P_2 on the supposition that $P_2(\infty) = P_1(\infty)$. The top number in the second column gives the value of μ and the lower the value of the denominator when $m = 1$, *i.e.*, the value of $1+\mu+\alpha$. Thus in NaP_1

$$\mu = 1{\cdot}148678 \pm {\cdot}000477 \text{ and the denominator of } P_1(1) = 2{\cdot}116902 \pm {\cdot}000070.$$

The variations are, of course, subject to the correct value of N being 109675 and to m being integral. Alterations in N or taking, say, m to be $m+{\cdot}5$ would produce further consequent alterations in A.

Relation (D).—An inspection of the values given for S (∞) and D (∞), with their possible variations, show that in all cases their values are the same within limits of observation.

Relation (E).—The equality of $P_1(\infty)$ and $P_2(\infty)$ is so far justified by the fact that its assumption in calculating P_2 gives constants which reproduce the observations within possible errors. There is, however, still room for doubt as to exact equality, owing to imperfection of data.

Relation (F).—Viz.: $S(\infty) = VP(1)$. If $S(\infty)$ be written in the form N/D'^2 and D be the denominator of P (1), this relation involves the equality of D and D′. The values are given in the table. From them we get the following values of D′−D:—

Na . . .	$\cdot000084 \pm \cdot000235$	Rb . . .	$\cdot000581 \begin{cases} -\cdot000624 \\ +\cdot000569 \end{cases}$
K	$\cdot000656 \pm \cdot001217$	Cs . . .	$\cdot000324 \pm$?

All are easily zero within limits of observational error. It will be further necessary to discuss whether the alterations called for will affect the permissible exactness of the formulæ for all the lines. Its discussion is bound up with that of the next relation.

Relation (G).—Viz.: $P(\infty) = VS(1)$. As before, write $P(\infty) = N/D'^2$. The table gives the following values of $D-D'$:—

Na . . .	·002772±·008390	Rb . . .	·010696+·016119 −·003210
K . . .	·009150±·008716		
		Cs . . .	·016712± ?

This at first sight appears distinctly against the truth of (G). Taking the actual errors of observation in the three lines used to calculate the constants of P to be respectively p, q, r times the possible amounts, and p', q', r' to be the corresponding ratios for the S series, the constants of the formulæ were determined in terms of them as explained before. Then the conditions (F) and (G) were imposed, and the question discussed whether it was possible to satisfy the equation by values of the p's, numerically less than unity. Starting with Na, the result was that it was impossible. As, however, this might be due to the fact that another term was required in the denominator, the work was repeated, using the formula $D = m+\mu+\alpha/m+\beta/m^2$. As we have seen above, NaS (6) is in all probability a bad reading. If this be put aside, it was found that it would be possible to satisfy the conditions and still bring in all the other lines within observational errors. For instance, putting $r = r' = p' = ·5$ and $q' = 0$ (p, q have inappreciable effect) gives

$$\text{For P, } n = 41446·44 - \mathrm{N} \Big/ \left\{ m + 1·149427 - \frac{·033851}{m} + \frac{·001352}{m^2} \right\}^2,$$

$$\text{,, S, } n = 24473·75 - \mathrm{N} \Big/ \left\{ m + \ ·652800 - \frac{·014424}{m} - \frac{·011695}{m^2} \right\}^2.$$

These satisfy both (F) and (G) exactly, and reproduce all the lines (S (6), of course, excepted) well within the limits of error. In S it is to be noted that the α, β are practically equal, and that β for P is negligible, *i.e.*, so small that a very small error in one of the determining lines would wipe it out.

The case of K was then discussed. Again, the relations could not be satisfied with the form $\mu+\alpha/m$, and the work was repeated with $\alpha/m+\beta/m^2$. As in the previous case, it was found possible indeed, but it was now necessary to take P (1) close to K.R.'s value instead of that of L. It could be done, for instance, by putting $p = ·11$, $p' = -q' = r' = -·35$, and $q = r = 0$. This gives

$$\text{For P, } n = 35006·05 - \mathrm{N} \Big/ \left\{ m + 1·296929 - \frac{·064312}{m} + \frac{·001909}{m^2} \right\}^2,$$

$$\text{,, S } n = 21965·21 - \mathrm{N} \Big/ \left\{ m + \ ·820947 - \frac{·025714}{m} - \frac{·025656}{m^2} \right\}^2.$$

These bring all the lines (P (5), S (2), excepted as before) well within the limits of error. Again, it is to be noted that in the S formula $\alpha = \beta$, and the β of P is negligible. The fact that this relation occurs twice suggests its being a real relation, and not due to the chance choice of the suitable values of p, q, r, &c. The limiting errors in the cases of Rb and Cs are so wide that it did not seem worth while to discuss them in the same detail, especially in view of considerations which will appear later. The evidence so far is strengthened as to the correctness of (F) and (G) in fact; but, on the other hand, the impression is intensified that there is something not quite correct with the form for the S series. RITZ uses $m+{\cdot}5$ instead of m, although there does not seem any experimental evidence in its favour. As a fact it can be shown that the use of $m+{\cdot}5$ in place of m in our formula makes it still more difficult to fulfil conditions (F) and (G).

(H). *The difference between the* μ*'s of* S *and* P.—If we write down the value of μ of P$-\mu$ of S, we get

Na	·492885± (5800)	or between	·498685	and	·487085
K	·470694± (6647)	„ „	·477341	„	·464047
Rb	·489489−(10578) + (6842)	„ „	·496331	„	·478911
Cs	·493306± ?				

·487 would include all except K. The values point to the possibility of there being a constant difference, if the correct S formula be found. Also it shows conclusively that such difference cannot be ·5, a supposition which has suggested the idea that the P and S are similar series, P with even numbers and S with odd. The supposition, moreover, is not borne out by the evidence of other spectra. It is very nearly ·5 in H, ·153 in He′, ·445 in O. The S (∞) is always very close to VP (1) wherever it can be tested. If this hold for Mg and Ca, the difference in their cases would be about ·34 for Mg and ·31 for Ca; Zn, Cd, about the same. There are clearly no valid grounds for the supposition in question.

(I). *The* D's *of* P.—A first inspection of the values of μ given in Table II. makes evident a remarkable approximate relation between the values of $\mu-1$ of the various elements. They may be written as follows:—

Na . . .	2[·074339±(238)]	Rb . . .	5[·073280±(228)]
K . . .	4[·074120±(373)]	Cs . . .	6[·075161± ?]

The possible variations show that, with the exception of Rb (which, however, very nearly falls in with the others), the values of $\mu-1$ are multiples of a number not far from ·074. The case is not really so strong as it looks, for the limits of variation are almost certainly much less than the maximum possible (which has been mentioned before). On the other hand, the relation is so close that a more correct value of N or the true form of the formula might well make the ratios exact. It is clear that the μ

have no direct relation to the atomic weight, but depend on some other physical property which obeys a similar law. In searching for such property it occurred to me to try the atomic volume, and I found an almost precisely similar relation for these. The densities of the alkalies are not so exactly known as those of other metals, and, moreover, they ought to be compared at corresponding temperatures. If, however, they are compared at about 10° to 15° C., and the values used which are given in LANDOLT and BÖRNSTEIN'S tables, viz.:—

Li = ·593 Na = ·9743 K = ·875 Rb = 1·52 Cs = 1·88

the atomic volumes come out as follows:—

Li = 11·81 = 1 × 11·81
Na = 23·606 = 2 × 11·80
K = 44·617 = 4 × 11·15
Rb = 56·05 = 5 × 11·21
Cs = 70·584 = 6 × 11·76

As the density of Cs is taken near its melting point it is too small, and we should expect a rather lower value for its atomic volume to compare with the others.

To settle whether the atomic volumes are multiples of the same number requires a more exact determination of densities. Mr. SWANN is at present investigating this question.

The values of $\alpha/(\mu-1)$ are

Na . . .	·2123 ± (6)	Rb . . .	·2035 ± (85)
K . . .	·2108 ± (75)	Cs . . .	·1997 ± ?

They indicate the same value for the ratio (·2120), but only by stretching Na and Rb to the extreme limits. It is noticeable that the ratio as determined from the most probable value continually decreases with increasing atomic weight.

When these relations were first observed the μ for K used had been determined on slightly different data, and the value of $\mu-1$ was 4 (·073984 ±), well within the maximum limits above. In this case the series of values of $\mu-1$ showed a superficial agreement with the atomic volumes, but it was not possible to correlate them with complete exactness. It was attempted to do so by adding a constant to $\mu-1$. It was then found to give good agreement if this constant were about ·014. In other words, add ·014 to the fractional part of μ and deduct it from the integral, *i.e.*, instead of writing $\mu = 1 + \mathrm{f}$, write $\mu = {·986} + \mathrm{f}$; then this fraction was proportional to the atomic volume. It will be remembered that the difference found between the μ's of the P and S series was about ·487, so that the μ's of P and S are of the form ·987 + f and ·5 + f. This agreement for about ·987 from two lines of agreement strengthens the case for each.

Again, if the values of $\alpha/\mathrm{f}\ (\mu = {·986} + \mathrm{f})$ be calculated, there results

Na . . .	·1951 ±	Rb . . .	·1951 ±
K . . .	·1975 ±	Cs . . .	·1937 ±

a much nearer approximation to equality than before; in fact, ·1950 well within all limits.

We are therefore led to surmise that the P series of all the alkalies can be represented by a formula,

$$\text{VS}(1)-\text{N}\Big/\left\{m+\cdot 986+k\times\text{atomic volume}\left(1-\frac{\cdot 195}{m}\right)\right\}^2,$$

the numbers inserted being only very roughly approximate. In other words, the knowledge of four constants (N, ·486 ± ? ·195 ± ? and k) gives all the lines of all the P series of the alkalies (Li not considered).

On the other hypothesis, viz., the excesses of μ over 1, exact multiples of a constant, and the ratio of $\alpha/(\mu-1)$ also a constant, $\mu+\alpha-1$ ought to exhibit a similar relation. Now $\mu+\alpha$ is determined with a far less error than either μ or α separately, and hence the values of $\mu+\alpha$ ought to show the relationships more clearly. The respective values are

Na . . .	$2[\cdot 058451\pm(35)]$	Rb . . .	$5[\cdot 058369\pm(3)]$
K . . .	$4[\cdot 058492\pm(264)]$	Cs . . .	$6[\cdot 060148\pm\ ?\ ]$

which is very strong evidence in favour of the multiple law for the first three at least.

The limits of possible variation are so close, the exactness of the equality within those limits so absolute, that there can be no doubt that the relation is an absolute law. We have found already that the same law is indicated for μ and α, but with greater deviations; in the case of Rb outside the permissible limits. It is clear, therefore, that the inequalities of μ and α must counterbalance one another when $m = 1$, *i.e.*, there is probably a term $x(1-1/m)$ in addition to the term $sb(1-c/m)$. (Here and for the future s stands for the integer proper to the particular element, 2, 4, 5, 6, b for the factor, and c for the constant ratio of α to $\mu-1$.) Later, evidence will be given of a new type of series (the F sequence) based on an atomic weight term which (and multiples of which), as will be seen immediately, determines the second (or second and third) of the doublet (or triplet) series. The values of these terms are determined in the next paragraph. If x in the above be taken, one-half of these values, and deducted, it will be found to give the perfect agreement required for Na, K, and Rb. If W denote this atomic weight term, W for the four elements are ·000370, ·001466, ·006444, ·016267, and the values of D for these elements are then $1-\text{W}(1-1/m)$ + the following terms :—

Na	$2\{\cdot 074524\pm(238)-m^{-1}[\cdot 016073\pm(203)]\}$
K	$4\{\cdot 074486\pm(373)-m^{-1}[\cdot 015992\pm(637)]\}$
Rb	$5\{\cdot 074569\pm\ (89)-m^{-1}[\cdot 016199\pm\ (85)]\}$
Cs	$6\{\cdot 077872\pm\ (?)\ -m^{-1}[\cdot 017724\pm\ (?)\ ]\}$

For the first three, the factors are easily equal within limits, say $\cdot074560-\cdot016120/m$. If we remember that the limits for Rb were based for P (1) on LEHMANN's estimates of error, which are rather too small, we may represent the degree of closeness of the above numbers by attaching a possible error of about (80). With the above numbers the ratio $\alpha/(\mu-1)$ is ·21521. The formula for Na, K, Rb, is therefore

$$\mu+\frac{\alpha}{m}=1-\mathrm{W}\left(1-\frac{1}{m}\right)+\cdot074560s\left(1-\frac{\cdot21521}{m}\right)$$

with uncertainties in the two last digits in each number. The new arrangement has, however, thrown Cs quite out of order. Not only is the factor too large, but the ratio of α to it is also too large, viz., ·2276. If the term in W be omitted

$$\mu+\frac{\alpha}{m}=6\,(\cdot075161\pm?)\left(1-\frac{\cdot2000\pm?}{m}\right).$$

To bring this into agreement with the above would require a change in μ of about ·003600, which might just be possible. As we shall see later, the series appear to depend on fundamental types in which $\mu=1-p\mathrm{W}$ where p are integral. It is just possible that in Cs the type changes from one to the other.

The preceding arguments may appear unsatisfactory, as they apparently lead to two different results with equal evidence, but there is reason to think that if the values for the atomic volumes are known with greater accuracy, they will be found to agree. If not, then the second argument stands, and the former falls, as based on incorrect values of the atomic volumes.

(J). *The* D's *of* P_2.—A glance at the table shows that the α are practically the same for both P_1 and P_2. The doublet separations, therefore, are due to a change in μ alone. In determining the values of $\mu_1-\mu_2$ use may be made of the values in the table; but as the doublet separations are much more accurately known than the wave-numbers of the lines from which the constants have been determined, it will be better to calculate the differences between the D's of P_1 and P_2 on this basis, assuming the D of P_1 (1) correct. Any small error in the latter will have an infinitesimal effect on the difference in question. Taking the following values of ν as the most probable,

$$\mathrm{Na}=17\cdot10\pm\cdot1,\qquad \mathrm{K}=57\cdot87\pm1,\qquad \mathrm{Rb}=236\cdot78\pm4,\qquad \mathrm{Cs}=552\pm2,$$

and taking N = 109675, there result for the differences of the D's of P_1 and P_2

Na.	K.	Rb.	Cs.
·000744±(4)	·002933±(50)	·012887±(215)	·032435±(116)

or

$\cdot01406\,(\cdot23)^2$	$(\cdot01920\pm(33))\,(\cdot3910)^2$	$(\cdot01765\pm(30))\,(\cdot8545)^2$	$(\cdot01839\pm(7))\,(1\cdot328)^2$

We might have expected that the differences would have come out proportional to the squares of the atomic weights. It is not so, however; nor is there a regular progression, as the order of increase is Na, Rb, Cs, K.

In the original calculation the limits of P_2 were found from the observations, and not by making $P_2(\infty) = P_1(\infty)$, except, of course, for Na, where only two lines of NaP_2 had been measured. In this case the difference of the D's of P_1 and P_2 involved α as well, and an inspection showed that the ratio of $\delta\alpha$ to $\delta\mu$ was about $\frac{1}{3}$ for K, $\frac{1}{4}$ for Rb, and $\frac{1}{5}$ for Cs. If this apparent rule be made exact and put in the form $kw^2[1-1/m(s-1)]$, where s, as before, denotes the element multiple, we find the following values of k:—

K. . ·01439±(22); Rb. . ·01412±(23); Cs. . ·01532±(6),

whilst the result for Na is $\cdot 01406w^2$ without a term in $1/m$. This points to the probability that the change in μ is accompanied with a change in α, and that the change in μ is a constant multiple of w^2, whilst the change in α depends in a more complex way on the properties of the element. The term $1-1/m(s-1)$ looks like a first approximation from a complete formula. In many cases, for instance, the form of denominator $m+\mu+\alpha/(m+\mu)$ reproduces the lines with great accuracy. If the μ were decreased by kw^2 the change in D would not be in a constant ratio to w^2, but would involve α and μ, *i.e.*, s. The doublet separation is given by the difference, when $m = 1$. In the approximation arrived at above it is $\cdot 0141w^2$ for Na, and $\cdot 0141w^2s/(s-1)$ for K and Rb, and Cs, but second order terms are required for the large w^2 of Cs.

(K). D's *of* S(∞).—Since the S(∞) are very close to VP(1), we should expect to find a similar relation between the D's of S(∞) as for the P series. The actual numbers are, writing down only the fractional parts,

Na = ·116986±(165) = 2 [·058493±(82)]
K = ·234625±(159) = 4 [·058656±(40)]
Rb = ·292398±(218) = 5 [·058480±(44)]
Cs = ·361214± ? = 6 [·060202± ?]

but there is here an additional uncertainty owing to the fact that, in calculating the S series, the means have been taken and the $S_1(\infty)$, $S_2(\infty)$ determined from their means by an estimated value of ν. The limits of the D series are much closer to the VP. Naturally, therefore, they bring out the relationship rather more clearly.

(L). *The* D's *of* S.—The μ's of S, as we have seen, suggest that we have to do with $\mu = \cdot 5+\text{f}$. If we write down the fractions, we get

Na . . . ·155793±(5368) = 2 [·077896±(2684)]
K . . . ·325786±(5155) = 4 [·081446±(1289)]
Rb . . . ·376910−(9438) +(5702) = 5 [·075382−(1888) +(1140)]
Cs . . . ·457661± ? = 6 [·076277± ?]

The numbers do not suggest the relationship so strongly as those of the preceding cases. The limits, however, are so wide that it is the only one in which the absolute identity of the common factor is possible without overstraining them.

The values of the α are for all the elements less than for the P series. They are, for the elements in order,

$$2[\cdot 01314 \pm (686)], \quad 4[\cdot 01190 \pm (346)], \quad 5[\cdot 01257 + (510) - (177)], \quad 6(\cdot 01200 \pm \ ?\ ),$$

or easily ·0120 within limits of error, but the limits are wide. The ratios of $\alpha/(\mu - \cdot 5)$ are ·0170, ·0140, ·0164, ·0140. They are not constant, but their irregularity points to a want of law in deviations from equality, or, in other words, that equality exists in the true formulæ. There seems something defective in the form for the S series, as has already appeared in its failure to give the first lines S (2), as well as to reproduce the values of P (∞) exactly.

The Diffuse Series.

The observations for the D series are not sufficiently exact to enable such certain conclusions to be drawn as in the case of the other two types. Besides, there seems at first sight to be a change of type as we go through the group of elements. Satellites clearly show themselves only in Cs. There is some indication of satellites in Rb, but, as we have already seen, there is considerable doubt as to their actuality. K shows no sign whatever of them. On the contrary, Na does, not by offering satellite lines themselves, but by a regular increase in ν as the order increases—a point already discussed under the remarks on Table I. The satellite series in general plainly suggest an analogy with the P series, in which the P_2 lines are satellites to the P_1, and it is natural to search for series whose limits are the $VD_1(1)$ and $VD_2(1)$ giving corresponding doublets. Working on this basis for the clearly defined satellite series of Cs (satellites for $D_1(3.4.5.6)$ observed), we get two values for the N/D^2 of the top lines of the formulæ determining them which give a separation of 97·07, and, as we shall see, determine the limits of an additional doublet series. The satellite series are more fully and more numerously developed in other elements than the alkalies, and their general discussion is better deferred until the other elements are discussed in a succeeding communication.

In determining the value of α the question arises whether μ should be taken to be a fraction or 1+f. If $\mu = \mathrm{f}$, $m = 1$ gives a line too far in the ultra red to have been observed. The observations of known lines by themselves are not sufficiently exact to decide the question—as, *e.g.*, in the P series. If we regard the doublet separation of an associated series as determined by the top lines of its principal series, then, as we shall see shortly, the evidence in the case of Cs points to the fact that the denominator of the top line $= 2 + \mathrm{f}$, *i.e.*, $\mu = 1 + \mathrm{f}$; but there may be some uncertainty here also in view of RYDBERG's suggestion that each V of a series may form the limit of a new series—*e.g.*, not only is there the sharp series VP(1)−VS, but there may also be VP(2)−VS. RITZ has given several examples of this. As the matter is thus open the formula as determined on each supposition is entered in Table II.

In the P and S series α is negative. It is positive in the D series, not only in the alkalies, but in other typical D series; in fact, so general is the rule, that if any new series gives α positive it may be taken at least provisionally as a D series.

(M).—If we write down the values of μ of P+μ of D and of $\mu+\alpha$ for D, we find the following:—

	$\mu_p+\mu_d$.	$\mu+\alpha$.
Na . . .	2·126987±(1164)	1·004918
K . . .	1·987273+(6592)	·997538−(17150)
	−(32938)	+(103360)
Rb . . .	1·987783±(14827)	·861570±(27275)
Cs . . .	1·980930± ?	·543920± ?

The numbers for Na look abnormal. We shall see later that the D series here belongs to a sequence of a new type, for which the notation F is proposed. It need not, therefore, be here further considered. The values of $\mu_p+\mu_d$ for the others point to a constant value, which suggests that μ_p is of the form A±B and μ_d of the form A∓B. Now we have seen that μ_p is of the form A−B. If we calculate the values of A+B we get the following values for K, Rb, Cs, using the mean value of b, viz., ·074560,

·700294, ·620756, ·536373.

The first two agree with the values found for μ, for K, and Rb well within the limits of error. The third is obtained on the supposition that the atomic weight term is W as for the others, and it is clearly too large. But in the P series we saw that apparently the W term had fallen out. If this missing term be put in here, *i.e.*, 2W deducted from unity in place of W, the value of μ comes out to ·520205, well within permissible limits of the μ of D_{21} or D_{12}. The μ of $D_{11}(2)$ is ·008168 greater than that of $D_{12}(2)$ as calculated from the observed lines (see Table II). Now ·008109 is $\frac{1}{2}$W. Hence, with the satellite series of Cs, the D's are given by

$$m+1-3W\left(1-\frac{1}{m}\right)-6b \qquad \text{for } D_{11},$$

$$m+1-4W\left(1-\frac{1}{m}\right)-6b \qquad \text{for } D_{12} \text{ or } D_{21},$$

the values for K and Rb being

$$m+1-W\left(1-\frac{1}{m}\right)-sb.$$

The cases of K and Rb, both for P and D, falling into analogous forms, while in that of Cs both P and D show a difference, although depending on the same kinds of constants, forms another argument in favour of the view that Rb and K actually do not possess satellite series like Cs. They have not been observed—not through the observer's fault, but because they do not exist.

The limits of errors are so much wider in the case of these series than in that of the P that the evidence in favour of the above is not, perhaps, so conclusive as for the latter. I think, however, that there can be no reasonable doubt that it is correct in the main. It is quite possible that, in place of unity from which the terms are deducted, the true quantity may be a number near unity for the alkalies.

The values of α are so uncertain that it is hopeless to expect to draw any safe conclusion from them, beyond this that apparently the simple law observed in the case of the P series does not now hold. For K the value of D is very close to

$$1-\mathrm{W}\left(1-\frac{1}{m}\right)-4b\left(1-\frac{1}{m}\right).$$

For Rb it may be written

$$1-\mathrm{W}\left(1-\frac{1}{m}\right)-5b\left(1-\frac{1}{m}\right)-\frac{\cdot 1384-(396)}{m}.$$

For Cs the α is very small for both satellites and practically equal, the D's differ only in μ. The constitution of α for D must therefore, unfortunately, with the extremely inexact measurements, be left unsettled at present.

Other Associated Series.

In discussing the remaining observed lines of the alkalies not included in the three typical groups, it will be simpler to take the elements in the reverse order, commencing with Cs.

Cs. The lines to be accounted for are the following, in which the letter refers to the observer :—

13711 B.	10127 B.	8082·02 L.	7280·5 S.	6872·6 S. 69 R.
	ν = 97·46	96·25	98·20	97·38
	10028 B.	8019·62 L. 7·1 S.	7228·8 S. 7·46 L.	6826·9 S. 9 R.
6630·5 S.	6475 S. 2 R.	6359 S.	5209 R.	
		84·51		
97·27	98·38			
6588 S.	6434 S. 3 R.	6325 S.		

In the above ν denotes the difference of wave-numbers of the lines above and below it, the top line being taken when two observers are in question. The pairs are recognised as forming a doublet series. We have seen that this value 97·1 is the difference between the $D_{11}(2)$ and $D_{12}(2)$ calculated from the formula, D (2) not having yet been observed. It is natural, therefore, to look to the D series as generating those in question in the same way as the S depends on the P, *i.e.*, the limits of the new series should be $VD_{11}(2)$ and $VD_{12}(2)$ or $VD_{21}(2)$, *i.e.*, about 17000. If we employ this, however, it is at once seen to be too large. If the lines 8082, 7280, 6872 are used to calculate the constants, there results

$$N = 16783{\cdot}52\,(+\nu)-N/(m+1{\cdot}038603-m^{-1}\times{\cdot}219539)^2,$$

which is of the S type. The formula does not look right, the limit is rather far from VD (2), and, moreover, it is the first case where there has appeared a value of $\mu-\alpha/m$ which passes from <1 to >1 as m increases. The formula which bounds, so to say, the change from the S type to the D type, *i.e.*, $\alpha = 0$, and satisfies the two lines 8082 and 7280 exactly, is

$$16810-N/(m+{\cdot}968295)^2,$$

and it gives a better agreement with the other lines, as is shown by the following table, in which only the values for the first of each doublet is given for the former formula. The differences are for obs.–calc. and ν is taken to be 97·5 :—

m.	3.	4.	5.	6.	7.	8.	9.
Form 1	– 63	0	0	0	1·45 S.	– 3 S.	– 12·8
Form 2	– 26·5 B.	0 L.	0 S.	1·36 R.	1·90 R.	– ·24 R.	– 7·15 S.
	– 26·5 B.			2·30 S.	·75 S.	– ·02 S.	– ·90 S.

For the last, the measurements of S give $\nu = 84{\cdot}5$ or 13 too small, *i.e.*, a wave-length difference 5·2 A.U. too small. If the second line is correct, showing good agreement with the formula, the first would therefore be –2 wrong instead of –7·15. As is seen, the second formula gives extremely good agreement. If the limit is higher than 16810 the series becomes a D type. In these inexact measurements, however, it is probably best to use RYDBERG's form without the α. Even now the limit is not that calculated for VD (2); there may be a small error in the latter, but hardly to the extent of 200. We may feel as certain, however, that the limit and VD (2) are the same as for the corresponding case of P (∞) and VS (1), in which the "error" is also considerable. The strongest evidence is in the striking fact that the D_{11} and D_{12} series generate the doublet separation. For $m = 2$, $\lambda = 22920$, which would be far outside BERGMANN's region of observation.

The only lines now left unaccounted for in Cs are 13711 B. and 5209 R. The wave-number of 13711 is 7291·4. $VD_{11}(2) = 17040$* roughly, $VP_2(2) = 31400-21764·7 = 9635·3$, so that $VD_{11}(2)-VP_2(2) = 7405$. There is just a possibility, therefore, that 13711 may be the latter; but, if so, it is curious that the P_2 should come in and not P_1, which we should expect to give a stronger line.

Rb. The lines to be accounted for are 13442 B., 10069 B., 8872 B., 8271 B., 8513·26 L., 6306·8 R., 5165·35 R., 4967 R., to which should possibly be added that hitherto supposed to be $D_{11}(3)$, viz., 7753·58 L.

The first four form a series. Using the first three for the constants, there results

$$n = 14295-N/(m+1·04968-m^{-1}\times·15177)^2.$$

This reproduces the fourth with an error 10 A.U., which is not excessive when the inexactness of the whole measurements is considered, but they are sufficient to settle that the limit is close to 14295. The value of VD(2) as calculated is 14270. BERGMANN's value for $D_1(2)$ has a wave-number 6487, which with the reliable value of $D_1(\infty) = 20876$ gives $VD(2) = 14389$, but we have seen that BERGMANN's value is probably considerably wrong. The evidence, however, is sufficient to indicate that Rb also has a series in which the limit is VD(2). The corresponding series in Cs was a doublet owing to the D series having satellites. The absence of duplicity here, therefore, favours the view put forward on other grounds, that RbD is not a satellite series. On the contrary, it is possible that, if there were a doublet series, the doublet separation would be too small for BERGMANN to have separated: for instance, he did not separate NaD(2), which he observed as one. The formula gives the next two lines to be 7938·6 and 7720·6. The first, allowance being made for its uncertainty, probably comes close to 7950, which is $RbP_2(1)$, and the latter may well be 7753, the line which has generally been taken to be $D_{11}(3)$, but which we have had reason to suppose not to belong to the D series.

The lines 8513·26 L., 6306·8 R., 4967 R. satisfy the equation

$$n = 21703-N\Big/\left(m+1·350891-\frac{·065154}{m}\right)^2 \text{ for } m = 2.3 \text{ and } 7.$$

The N/D^2 is practically the same as for the P_2 series. The missing members should be at 5602, 5270, 5084. The first has not been observed, the others are in the neighbourhood of $D_1(7)$ (5260) and $D_2(8)$ (5089 R. or 5088 S.). The limit $21703 = N/(2·2481)^2$, so that it is not apparent how it arises. The arrangement does not give much confidence, although the connection with P_2 is curious.

Of the other line, 5165 R., SAUNDERS has pointed out that it is near the edge of a carbon bond, and is therefore a doubtful Rb line.

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* 17040 is extrapolated from a not very accurate formula. $VD_{11}(2)$ is probably somewhat greater than the limit in the series just discussed, viz., 16810, making $VD_{12}(2)$ about 16910, which would give $VD_{12}(2)-VP_2(2) = 7275+?$ agreeing.

K. The K lines to be accounted for are the following:—

	27215·0	P.	4829	R.
	27065·6	P.	4808·8	L.D.
F	15165·8	P.	4767	R.
F	11028·0	P.	4642·35	R. }
F	9590	B.	·5	S. }
F	8908	B.		
F	8500	B.	4638·6	R.
F	7931·8	S.		

The lines marked with F form one series. The constants calculated from the first three (third inexact) give

$$13522{\cdot}81 - N/(m + {\cdot}907393 + m^{-1} \times {\cdot}211692).$$

This reproduces the lines with the following values of obs. − calc.:—

m	3	4	5	6	7	8	9	10
	0	0	0	22·5	14·9			·27

The lines corresponding to $m = 8.9$ would be 8232·9, 8059·6, which lie below Bergmann's lowest region of observation and Saunders' upper limit. Paschen's two observations are good, Bergmann's may quite possibly err to the amount indicated.* There can be no doubt about the series—the formula is only doubtful in so far as the third line from which it is determined may be several units out. The value of the wave-number of D (2) is by Paschen's observation 8496·63 ± ·36. The limit of the D series is 21966·82 ± 6·64 (see Table I.). Hence the value of VD (2) is $21966{\cdot}82 \pm 6{\cdot}64 - 8492{\cdot}63 \pm {\cdot}36 = 13474{\cdot}19 \pm 7$. The most probable value is $21972 - 8492 = 13480$. The limit of the series as found is so close to this that there is some justification in taking it to be exactly so. If this be assumed, there are three reliable data to go upon, viz., Paschen's two lines and the limit. These give the formula

$$n = 13480 - N/(m + {\cdot}966367 + m^{-1} \times {\cdot}071808)^2,$$

giving the following values of obs. − calc.:—

0	0	−10	+4	−3·8	−22

The agreement is much better for Bergmann's lines, but the last is too far out to allow 7931·8 to be included in the series, nor can this be set down to uncertainty in the constants if the supposition of limit = VD (2) is exact for the kind of formula. If it be remembered that, so far as the matter has been yet considered, the value of P (∞) is never exactly VS (1), and that a similar cause for the apparent difference may occur here, we may still hold that in fact the limit is the true VD (2), but that the first formula is the most correct to use with the actual form of the formula

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* *E.g.*, in the lines 27215 and 27065 his differences from Paschen were − 116 and 16.

(which involves a particular value of N). This gives a better agreement, and clearly brings 7931 into the series. If we employ RYDBERG's formula,

$$n = 13458 - \mathrm{N}/(m + \cdot 99667)^2,$$

with errors 0 0 −15 −4 −13 −14·4,

clearly the limit is too low. PASCHEN has pointed out that 27065·6 and 27215 are respectively $\mathrm{VP}_1(2) \swarrow \mathrm{VS}(2)$ and $\mathrm{VP}_2(2) \swarrow \mathrm{VS}(2)$. How closely this is the case may be illustrated by calculating these values with the limits of errors. $\mathrm{VP}_1(2)$ and $\mathrm{VP}_2(2)$ are 10286·84 and 10305·59, with possible errors 1·73. Using the calculated limits of the D series (Table I.) and PASCHEN's value of S (2), the value of VS (2) is 13980·16 ± 3·82, giving respectively from the above relations 3693·32 ± 5·5 and 3674·57 ± 5·5. The wave-numbers of the actual lines are 3694·02 ± ·14 and 3673·74 ± ·27. Still it is a single agreement, and might possibly be fortuitous. The measurements of wave differences are much more reliable than those of actual wave-lengths. Now the difference for the two lines in question gives $\nu = 20 \cdot 28 \pm \cdot 41$, with PASCHEN's estimates of his errors. The difference for $\mathrm{P}_1(2)$ and $\mathrm{P}_2(2)$ is 18·75 ± ·36, which is decidedly against the conclusion. In favour of it, on the other hand, is the fact that a similar relation shows itself under Na. There is another unallotted pair, 4642·35 R. (·50 S.) and 4638·6 R., with a separation $17 \cdot 40 \pm 4 \cdot 5\, d\lambda$, where $d\lambda$ denotes the wave-length difference error of observation. The first has a wave-number about $\mathrm{P}(\infty) - \mathrm{VD}(2)$, viz., $21534 \cdot 92 \pm 4 \cdot 5\, d\lambda$ as against 21532 ± 7. It is difficult to see where a doublet with ν about 17 to 20 could come in unless the D series was a satellite one, in which case the first series here considered should be a doublet one. If so, however, it would have been seen by PASCHEN, who separated much closer lines in the ultra-red Na spectrum. The other lines left over are 4829 R., 4808 L.D., and 4767 R.

Na. The lines observed in Na not belonging to the regular series are much more numerous than in the other elements. The following is the list:—

	23391·3	P.
	23361·0	P.
	22084·2	P.
	22056·9	P.
F (3)	18459·5	P.
F (4)	12677·6	P.
G_1 (2)	7418·3	S.
G_2 (2)	7410	S.
A_1 (2)	7377·4	S.
A_2 (2)	7369·4	S.
B_1 (3)	5675·92	K.R.
B_3 (3)	5670·40	K.R.
A_1 (3)	5532·7	S.
	1·7	K.H.
A_2 (3)	5528·2	S.
	7·1	K.H.
G_1 (3)	5100	LE.
	4975·0	S.
B_1 (4)	6·1	K.H.
B_2 (4)	4973·0	K.H.
A_1 (4)	4918·4	S.
A_2 (4)	4914·0	S.
E_1 (4)	4913·5	K.H.
E_2 (4)	4910·1	K.H.
	4820	LE.
	4730	LE.
B_1 (5)	4660·2	S.
	·0	K.H.
A_1 (5)	4633·1	K.H.
A_2 (5)	4629·4	K.H.
E_1 (5)	4629·5	S.
E_2 (5)	4625·5	S.
E_1 (6) G_1 (4)	4472·5	S.
A_1 (6)	0·0	LE.
A_1 (7)	4372	S.

From analogy with the preceding elements it is natural first to seek for the presence of a series whose limit is VD (2). This is

$$24467{\cdot}09 \pm 2{\cdot}77 - 12199{\cdot}58 \pm 2 = 12267{\cdot}51 \pm 4{\cdot}77.$$

The lines 18459, 12677 fall in with this, but no others of the series have been found. If the limit is actually 12267 the formula can be found at once. In all the other cases, however, it has been slightly different. It will, therefore, be best to use the old RYDBERG formula, whence

$$n = 12275{\cdot}3 - \mathrm{N}/(m + {\cdot}998613).$$

The next three lines given by this are λ = 10837, 9963, 9469, but these come in a region in which there are no records. It is below BERGMANN's lowest and SAUNDERS' highest. The limit falls about 8147, close to 8210, where SAUNDERS observed a faint group. The latter might, therefore, represent the last faint lines visible.

The four lines above these in the list are doublets $\nu = 5{\cdot}54 \pm 3{\cdot}28$ and $5{\cdot}50 \pm {\cdot}92$. PASCHEN points out that they satisfy the relations $\mathrm{VP}_1(2) - \mathrm{VD}(3)$, $\mathrm{VP}_2(2) - \mathrm{VD}(3)$, $\mathrm{VP}_1(2) - \mathrm{VS}(2)$, $\mathrm{VP}_2(2) - \mathrm{VS}(2)$. To test this, as in the case of K, $\mathrm{P}(\infty)$ is $41446{\cdot}76 \pm 1{\cdot}69$, $\mathrm{P}_1(2) = 30271{\cdot}83 \pm {\cdot}27$, $\mathrm{P}_2(2) = 30266{\cdot}33 \pm {\cdot}27$, $\mathrm{D}(\infty) = 24474{\cdot}13 \pm 3{\cdot}48$, $\mathrm{D}_1(3) = 17575{\cdot}28 \pm {\cdot}46$. Hence $\mathrm{VP}_1(2) = 11174{\cdot}93 \pm 1{\cdot}96$, $\mathrm{VP}_2(2) = 11180{\cdot}43 \pm 1{\cdot}96$, $\mathrm{VD}(3) = 6898{\cdot}85 \pm 3{\cdot}94$, $\mathrm{VS}(2) = 15705{\cdot}69 \pm 4{\cdot}61$, whence the wave-numbers compared with observed would be

Calc., $4276{\cdot}08 \pm 8{\cdot}90$, $4281{\cdot}58 \pm 8{\cdot}90$, $4528{\cdot}26 \pm 6{\cdot}57$, $4530{\cdot}76 \pm 6{\cdot}57$;
Obs., $4273{\cdot}98 \pm 1{\cdot}82$, $4279{\cdot}52 \pm 1{\cdot}46$, $4526{\cdot}94 \pm 0{\cdot}51$, $4532{\cdot}55 \pm 0{\cdot}41$.

Here also, contrary to the case in K, the test as to doublet separation holds. The observed ν for the P (2) lines is $5{\cdot}50 \pm {\cdot}54$, agreeing with the separations in this case.

The lines marked with A in the list form a doublet series—ν about 14·7—which has been called LENARD's series, who first discovered some of the lines, later measured by K.H. and by S. The lines were arranged in the above order by SAUNDERS, who, however, could not fit in any of the usual formulæ for it. The readings are too uncertain for any definite assertion. If the first three corrected to constant $\nu = 14{\cdot}8$ be used to determine the constants, each of the second doublet being means of K.H. and S., the resulting formula is

$$n = \underset{85{\cdot}4}{24570{\cdot}6} - \mathrm{N}/(m + 1{\cdot}013864 + m^{-1} \times 281906),$$

giving the following values for obs.−calc. :—

$m = 2$	3	4	5	6	7
0	0	0	−·1	1	2·5

taking SAUNDERS' values, except for the last but one, where LENARD's is taken, SAUNDERS' reading would give a difference about 2·5 greater, or 3·5.

When we consider the remainder, considerable difficulty arises owing to the number of ill-defined lines so close together. In some cases K.H. and S. give very discordant readings for doublets, which yet are so close that they look as if the measurements might refer to the same lines, whilst in other cases the same observers agree much more closely. It is to be remembered that apparently the method of illumination has a great deal to do with the development of some of these lines in the spectra—in fact, they appear to come from different sheaths of the flame or arc, as if it were a question of temperature. The doublet at 5675 was observed by K.R., and was the only observation of theirs which did not fit in with the ordinary series. It is peculiar in being diffuse towards the violet. Diffuseness to the red is a general peculiarity of the diffuse series. If we look for the seat of this diffuseness in the formula, it would appear to lie in the VD part of the formula through diminishing denominator. If a series were such that the VD came to the limit—as, for instance, in many of the new series—the VD would be additive instead of subtractive, and the change in the denominator would now produce a diminishing wave-length or diffuseness towards the violet. RYDBERG's tables show that this doublet 5675, the doublet at 4976 K.H., and 4660 range near his formula. They give, if K.H.'s value for the second is taken,

$$n = 24558{\cdot}0\ (+\nu) - \mathrm{N}/(m + {\cdot}89484 + m^{-1} \times {\cdot}2369)^2\ (\nu = 14{\cdot}7,\ 12{\cdot}1),$$

m being respectively 3, 4, 5.

On the contrary, if we take 7418 S., 5675 K.R., and 5100 LE., we get a series including in addition 4820 LE., 4660 S. As LENARD's readings were very rough, we may take the first and the last. There results

$$n = 23491{\cdot}5 - \mathrm{N}/(m + 1{\cdot}33977 - m^{-1} \times {\cdot}06153)^2,$$

giving for obs. – calc. :—

0 0 5·3 2·6 0,

which is sufficiently good agreement. The lines 5100 and 4660, however, have been observed by LENARD alone, and neither by S. or K.H. It does not look as if such lines, if really Na, would come next to so marked a line as 5675 K.R. The allocation of these lines to one series is therefore very doubtful. It is against the former that no other lines come in (a preceding line should be about 8025, and not likely to have been observed if existent); but, on the contrary, the nature of the lines is more correspondent, and it should be noted that the limit is within the limits of error of the LENARD series. If the apparent agreement is real, the limit would be very close to 24558 in both cases. If the LENARD series be recalculated with the limit 24552·6*

$$n = 24552{\cdot}6\,(+\nu) - N/(m + 1{\cdot}02583 + m^{-1} \times {\cdot}2631)$$

giving obs. − calc. :—

0 0 −1 S., +1·3 K.H., 1·1 S., −·13 S.,
−2·2 S.

making the fourth lie between the readings of K.H. and S. The agreement is improved.

There remain

$\left.\begin{matrix}7418{\cdot}3\\7410\end{matrix}\right\}$ S., 5100 Le., 4820 Le., 4730 Le.,

and possibly the doublets in which K.H. and S. disagree,

$\left.\begin{matrix}4913{\cdot}5\\4910{\cdot}1\end{matrix}\right\}$ K.H. $\left.\begin{matrix}4633{\cdot}1\\4629{\cdot}4\end{matrix}\right\}$ K.H.

Of these, 4913, 4633, 4470 are shown by RYDBERG's table to have a limit about 24466, *i.e.*, the S. and D. series and D's respectively 5·155, 6·155, 7·155, which clearly refer to the D's of VP. To test this, find the differences between the wave-numbers of these lines and the corresponding values of P_1 (4.5.6), and suppose K.H. and S.'s values may have observational error 1 A.U. and LENARD 5.

Obs. for the P_1	37296·20	±1·39		38539·51	±1·48		39298·90	± 1·54
K.H.	20346·55	±4 $d\lambda$	K.H.	21577·90	±4·6 $d\lambda$	Le.	22365·2	± 5 $d\lambda$
S.	24·37		S.	94·67		S.	52·69	
K.H.	16949·65	±5·4		16961·61	±6	Le.	16933·7	±26
S.	16971·83			16944·84			16946·21	± 6·5

The numbers would seem to show that where K.H. and S. give doublets not quite the same, that of higher wave-number must be taken. The differences are of about equal value, and their mean is 16946·9 = 16947±6; using this for other lines gives :—

P_1 (2).	P_1 (3).	P_1 (7).
30271·83	35041·93	39793±3
16947	16947	16947
13324±6	18095±6	22846±9

13324 has not been observed, 18095±6 is near the LENARD 18084±3, 22846±9 is also near the LENARD line 22866·5 S. (λ = 4372). The limit of the series is

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* It was originally done with this, and nothing is gained by recalculation.

$P_1(\infty) - 16947 \pm 6 = 41446{\cdot}76 \pm 1{\cdot}69 - 16947 \pm 6 = 24500 \pm 7{\cdot}5$, say. This, of course, suggests the same limit as the S. and D. series, which is $24472{\cdot}11 \pm 3{\cdot}84$. But the limits of error show that this is not the case, but that the difference is real. The limit of S_2 is 17·1 higher, or $24489{\cdot}21 \pm 3{\cdot}84$. Another 17·1 higher would give $24506{\cdot}31 \pm 3{\cdot}8$. In view of the actual limit $24500 \pm 7{\cdot}5$, we might provisionally fix it at 24506. The second line of the doublet would then be 24523·1. An additional 17·1 lands us on 24540·1, which is close to the 24550± ? of the two series considered above. These results can hardly be fortuitous. The limit of S_1 is generated by the P_1 series, being $VP_1(1)$; the limit of S_2 is found from this by deducting the atomic weight term, 2W, from the μ of $P_1(1)$. The limits will therefore be generated by writing $\mu = {\cdot}148678 - 2pW$ in P_1, where p has integral values from 0 to 5, and possibly to 7 (LENARD's series), both inclusive. RITZ has given the doublet series just considered as $VP_1(1) - VP_1(m)$, $VP_2(1) - VP_1(m)$. We have seen, however, that this cannot be the case.* Moreover, $VP_1(1) - VP_1(m)$ for $m = 1$ would give an infinite time of vibration, and would suggest instability. In fact, the configuration giving this series, containing one very long period, is apparently very slightly stable. It is possible that the $VP_1(m)$ ought also to be slightly different, but the observations are far too inexact to settle this.

Again, RYDBERG's tables show that 7418 S., 5100 LE., 4472 S. have denominators about 2·845, 3·845, and 4·845, with a limit 27026. Working from this they satisfy the formula

$$n = 27034{\cdot}5 - N/(m + {\cdot}8358 + m^{-1} \times {\cdot}0148).$$

27034 is not far from the value of VD (1), which is 27282 ± 52. But the interest of this allocation lies chiefly in this, that its μ is of the form we should expect for the real D series, if NaD were formed on the same plan as for K, Rb, Cs, in which we have seen that the μ is $1 - W - sb = {\cdot}8505$ with α undetermined. The closeness of the agreement is chance; the errors in observation are too great to give μ with certainty, but it is suggestive.

It will be convenient, for reference, to attach letters to the various series just considered. In the list the LENARD series is denoted by A, the second by B, the third by C, although a very doubtful one, that parallel to P by E and the last by G.

Collecting, we find

$$\begin{array}{ll} VP_1(2) - VD(3) & VP_2(2) - VS(2) \\ VP_2(2) - VD(3) & VP_1(2) - VS(2) \end{array}$$

$$F \equiv 12275{\cdot}3\ \{VD(2)\} - N/\{m + {\cdot}998613\}^2\ (m = 3{\cdot}4)$$

$$A \equiv \left.\begin{array}{r} 24570{\cdot}6 \\ +\nu \end{array}\right| - N \Big/ \left\{m + 1{\cdot}013864 + \frac{{\cdot}281906}{m}\right\}^2\ (m = 2.3.4.5.6.7)$$

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* Unless 4472·5 S. is 4 A.U. in error, which is not likely.

$$\mathrm{B} \equiv \begin{array}{r|}24558\\ +\nu\end{array} -\mathrm{N}\Big/\left\{m+\cdot 89484+\frac{\cdot 2369}{m}\right\}^2 \quad (m = 3.4.5)$$

$$\mathrm{E}_1 \equiv \mathrm{S}_1(\infty)+2\nu-\mathrm{VP}_1(m)$$

$$(m = 4.5.6)$$

$$\mathrm{E}_2 \equiv \mathrm{S}_1(\infty)+3\nu-\mathrm{VP}_1(m)$$

$$\mathrm{G} \equiv 27034\cdot 5-\mathrm{N}\Big/\left\{m+\cdot 8358+\frac{\cdot 0148}{m}\right\}^2 \quad (m = 2.3.4)$$

$$\mathrm{C}\,?\!\equiv 23491\cdot 5-\mathrm{N}\Big/\left\{m+1\cdot 3398-\frac{\cdot 0615}{m}\right\}^2.$$

All the terms in α/m have little significance, as the lines are too uncertain to enable α to be determined with any approximation. The only lines not allocated are LENARD's 4820, 4730, which have not been seen by any other observer.

Comparison of the Different Elements.—The first certain result is the appearance of a strong well-developed series in the ultra-red, whose limit depends on the value of VD(2), giving doublet series when VD has two values as in Cs. The limits, as calculated from three observed lines, differ from the exact values of VD by amounts increasing from Na to Cs in somewhat the same way as in the corresponding cases of VP(1) and S(∞), and will probably be accounted for in a similar way. If the limits are taken to be VD(2) exactly, the resulting formulæ are of the D type, as found from two lines. Na and K give the D type, Rb and Cs the S type.

The observations are not sufficiently accurate to definitely settle this question. Under the circumstances it may be best to use RYDBERG's formulæ, *i.e.*, $\alpha = 0$. In this case the μ is always not far from unity, and the limits are closer to VD(2). The values of μ for Na, K, Rb, Cs come out respectively ·9986, ·9965, ·9798, ·968, the first two only being reliable as deduced from PASCHEN's observations. Taking his estimates of observational errors, the values for Na and K are respectively $\cdot 998610-\cdot 000343p+\cdot 002986q$ and $\cdot 996648-\cdot 000519p+\cdot 000735q$ where p, q are the fractions of his possible error.

It is seen that they may possibly be equal, and the possible errors for Rb and Cs do not contradict, that they also may have the same μ—say, about ·997. Its possibility, also, may be further illustrated by finding the difference of wave-numbers between the lines of K, Rb, Cs for $m = 3$ and $m = 6$, which have been measured for all three.

K	$11222\cdot 84\pm 1\cdot 26b-6592\cdot 00\pm\cdot 87 = 4630\cdot 84\pm 21,$
Rb	$12087\cdot 17\pm 1\cdot 46b-7437\cdot 36\pm\cdot 53b = 4649\cdot 81\pm 32,$
Cs	$14554\cdot 22\pm 8 \quad -9871\cdot 92\pm\cdot 97b = 4682\cdot 30\pm 24,$

b denotes B.'s possible error. It has been taken about 16—his actual error as against PASCHEN in KF(4).

It was my first impression that this would be the same for all the alkalies and the ·987 of the earlier discussion. It would be the basis of a fundamental series for each element, and the letter F which has been attached to it had its origin in this idea. But Ritz, who has discussed these series very fully and compared with those in other elements, proposes to represent the denominators by the difference of the denominators of the P_1 and P_2 series. At first sight this may appear a fanciful relation, but if it be remembered that this difference is merely the atomic weight term, whose subtraction from the atomic volume term in P_1 gives the D of P_2, the supposition is quite reasonable. His proposal, then, comes to this: to put $\mu = 1-2W$ where 2W is the atomic weight term. Now, the values of 2W are about ·000744, ·002933, ·012887, ·032435, their differences from unity giving (to four figures) ·9993, ·9971, ·9871, ·9676, which march closely with the values of μ obtained from the lines as observed. There is something to be said, therefore, in favour of the view that the value of μ for this series is 1 − atomic weight term, though it cannot yet be regarded as certain, against the supposition of constancy. The following table is interesting as throwing light on this point. It gives the differences of wave-numbers between successive lines for the elements indicated:—

Table III.

	2–3.	3–4.	4–5.	5–6.	6–7.	7–8.	8–9.
Li	5343·20 ± ·55	2470·05 ± 1·64	1342·27 ± 2·47	809·46 ± 35	538·39	353·71	
Na		2470·02 ± 5·5					
K		2473·42 ± 2·1	1359·29	798·13	538·68		
Rb		2491·44	1339·57	818·80			
Cs		2497·82	1361·80	814·96	531·17	362·10	281·66
H	5331·50	2466·95	1341·40	807·82	525·07	358·92	257·96
He	5342·84	2472·59	1342·88	809·48	525·31	360·11	257·39

What indication of change there is, is that there is an increase with increasing atomic weight. It is just possible, however, that they might be the same as the possible limits of error inserted below each number shown. Where no number is inserted (H and He excepted) the limits are very large, but no definite values can be assigned. At the same time the evidence is in favour of Ritz' theory. In accordance with what has been learnt as to the formation of the P and D sequences, I was inclined to think that the true denominators of the F sequence were $m+1-2W\left(1-\frac{1}{m}\right)$, the alkali P and D series depending on its second term, $m = 2$, giving $1-W$ for the basis of the P and D. Such a form agrees well with the observed lines for Rb and Cs where the measures are not exact. When, however, it is applied to Paschen's observation of the two first lines ($m = 3, 4$) in Na and K, it is seen not to hold, within at least PASCHEN's estimates of his errors (possibly underestimated as compared with K.R.'s scale), but that RYDBERG's form gives much closer approximation. Thus, for Na with $\mu = \cdot 999260 + \frac{\cdot 000740}{m}$, the differences of wave-numbers for F(3.4), taking F(∞) = 12272·24, would be 0, 1·60, and without the α term with F(∞) = 12273·08 they would be 0, ·77, both within the limits of error (4·97) for the second line. The value of the limit is nearer VD(2) in the first case. There is nothing to decide between the two theories here. But a similar treatment for K, where $\mu = \cdot 997067 + \frac{\cdot 002933}{m}$, gives in the first case with F(∞) = 13454·28 differences ·88 and −2, both close to PASCHEN's estimates of error (·88 and 1·23), whilst without the α term and F(∞) = 13456·73 the differences are 0, −·84. This definitely points to the RYDBERG form as the preferable one. On the other hand, with Cs, $\mu = \cdot 967565 + \frac{\cdot 032435}{m}$, where the α term is large enough to be really important, agrees better with the whole set of observations. Comparing the wave-length differences with those for the RYDBERG form we get the following table:—

RYDBERG .	−26·5 B.	0 L.	0 S.	4·96 S.	1·95 S.	−2·76 S.	−2·0 S.
α term . .	1·0 B.	1·5 L.	−1·3 S.	0	−·52 S.	−·08 S.	−3·8 S.

For Rb, $\mu = \cdot 987113 + \frac{\cdot 012887}{m}$, giving

RYDBERG . .	5·2	−4·7	4·5	0
α term . . .	18	−·4	5·4	0

Thus, as between the two suppositions, Rb gives no indication; Cs is in favour of α, and its large value of α makes it important, but it is not decisive; Na is satisfied by both, but is better for RYDBERG; K is the only one strongly in favour of RYDBERG. The question must therefore be left open at present, with leaning in favour of RYDBERG.

The validity of the supposition, that lines exist whose wave-number is the difference of the V part of the wave-numbers of two other lines, may be regarded as fully established by RITZ,* who calls it the Principle of Combination. Examples have occurred amongst the lines just discussed. It is possible, however, that what really happens is not an addition of unity to m, but an addition of our alkali constant. ·987? to the μ, *e.g.*, while we write a new limit as $N/(2+\mu)^2$, it may actually be $N/(1+\mu+\cdot 987)^2$. To settle this requires greater accuracy in the obscure lines than is to hand.

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* "Ueber ein neues Gesetz der Serienspektren," 'Phys. Z.,' vol. 9, p. 521.

It appears that, whatever the kinetic configuration may be which is the source of the vibrations, the light periods depend on the difference of frequency of *two* systems, each with distinguishing train of frequencies. This train, or sequence, we have denoted in the foregoing by putting the letter V before the letter representing the series. In what succeeds we will refer to them as the P-sequence, S-sequence, and so on. We recognise four typical sequences, the P, S, D, and the new F type. The evidence adduced in the preceding goes to show that the F type is the fundamental or primitive type. The P is formed from it by adding $sb\left(1-\frac{c}{m}\right)$, where b, c are constants, *or* atomic volume term $\times(1-m^{-1}\times{\cdot}195\,?)$, the D by deducting the same term or the atomic volume term, with some as yet unknown law for the term in α/m. The S term is found roughly by deducting a constant from the μ of P. The theory will fall in, as we shall see, with the Li, H, and He spectra also. Regarded from this point of view, we may look upon P as standing for positive, D for difference, and S for semi.

Lithium.

It is now time to take up the discussion of the spectra of lithium in the light of the knowledge gained from the consideration of the other alkali metals. The spectra of Li have been arranged like the others in three typical series, called the P, S, and D series. Taking these letters at present to stand for the arrangement hitherto accepted, and using the first three lines of each to calculate the constants, there result the following formulæ :—

$$\text{P} \;.\;.\; n = 43482{\cdot}20 \pm 1{\cdot}18 - \text{N}/\{m + {\cdot}951609 \mp (318) + m^{-1}\times[{\cdot}007365 \pm (262)]\}^2$$

$$\text{S} \;.\;.\; n = 28579{\cdot}44 \pm {\cdot}54 - \text{N}/\{m + {\cdot}602191 \mp (389) - m^{-1}\times[{\cdot}013039 \mp (735)]\}^2$$

$$\text{D} \;.\;.\; n = 28579{\cdot}99 \pm 4{\cdot}52 - \text{N}/\{m + 1{\cdot}000845 \mp (3274) - m^{-1}\times[{\cdot}005394 \mp (5457)]\}^2$$

The first glance shows at once that the lines ascribed to the P series follow a D type, and those of the D look like a P type. Also the values of the constants are very different from what we should be led to expect from the relationships discovered amongst the other elements. We should all the more expect to find these relations to hold, since Li falls in so closely with the analogous relationships for the atomic volume. In the above formulæ

$$\text{D of P}(\infty) = 1{\cdot}588172 \mp (21) \qquad \text{D of P}(1) = 1{\cdot}958974 \pm (23)$$

$$\text{D ,, S}(\infty) = 1{\cdot}958993 \mp (13) \qquad \text{D ,, S}(1) = 1{\cdot}589152 \pm (354)$$

$$\text{D ,, D}(\infty) = 1{\cdot}958980 \mp (115) \qquad \text{D ,, D}(1) = 1{\cdot}995451 \pm (2183)$$

It follows at once extremely closely that the laws (D), (F) hold, viz.,

$$\text{D}(\infty) = \text{S}(\infty) = \text{VP}(1),$$

also (G) is nearly so. We note that Li agrees with the other elements in making $P(\infty) \neq VS(1)$, and it differs also in the same direction.

The form of VD recalls at once the formula for the F sequences found in Cs and Rb. In fact, a Rydberg form would well serve it. To test this we can find the differences in successive wave-numbers. They are entered in the table above with the other elements, and an inspection leaves no doubt but that here we have the F type. VP is clearly a D type, although we should have expected the μ to be somewhat smaller. The third series is thus $VD(1)-VF(m)$, and the first $VS(1)-VD(m)$. The usual D series, however, gives $n = VP(1)-VD(m)$, and we ought to expect to find it. Now, certain additional lines have been observed by K.H. and S., viz., 6240·3 S., 4636·3 S., 4148·2 S., 3924 K.H. If they are the series in question their wave-numbers ought to differ by the same amount from those of the corresponding lines in the old P. The differences are 14904·73±2·8, 14903·93±2, 14914·10±10, 14905±15. In finding these the means of K.H. and S. were used, except for the last, which S. has not observed, but Exner and Hashek have. The permissible errors have been taken twice the difference of the readings of each two observers. The difference is close to 14904. Since the limit of the old P is 43482·20, the limit of the present is the difference or 28578±, the same as for the old S. and D. It should clearly be the same. Hence the formula is

$$28580-N/(m+\cdot 951609+m^{-1}\times\cdot 007365),$$

the ordinary D type.

In all the other elements we have met with series of the F type with limit VD (2). Now VD (2) (extrapolated from the formula) is 12557, and lines of the new series, if existent, ought to have wave-numbers $28580-12557 = 16023$ below those of the old D. The wave-numbers calculated in this way would be 5699, 8169, 9511, 10321, 10859, subject to uncertainties of a few units owing to the want of exact knowledge of VD (2). The first two lines clearly appear in Paschen's list of new ultra-red lines with wave-numbers 5695·95 and 8173·22, or λλ17551·6 and 12232·4.

There are two lines of Paschen's 18697·0, 12782·2, whose difference of wave-numbers is 2474·26. Table III. shows that they must have reference to the F sequence, and must be of the form

$$A-VF(3) \text{ and } A-VF(4).$$

The actual values of their wave-numbers give $A = 12202 = N/(2\cdot 9980)^2$.

Now the D of $F(2) = 2\cdot 998148$.

Hence these two lines are $VF(2)-VF(3)$ and $VF(2)-VF(4)$.

There are no apparent signs of series of the positive type. If we apply the multiple laws deduced in the foregoing we should get for the D of P

$$m+1+\cdot 074560-\frac{\cdot 016120}{m}-\cdot 000040\left(1-\frac{1}{m}\right)$$

taking the atomic weight term as about $\frac{1}{9}$ that of Na, *i.e.*,

$$\mu = 1\cdot074520 - m^{-1} \times \cdot016080,$$

giving

$$\text{VP}\,(1) = 25885 = \text{S}\,(\,\infty\,).$$

The μ of the S would be about ·005 more than $\mu - \cdot5$ of P, and the α about ·8 that of P, judging from analogy with the other series, *i.e.*,

$$\mu = \cdot5795 - m^{-1} \times \cdot0130,$$

whence

$$\text{VS}\,(1) = 44693 = \text{P}\,(\,\infty\,), \qquad \text{VS}\,(2) = 16566.$$

The values for D are more difficult to estimate, owing to uncertainty as to the α/m. The $\mu = 1 - \cdot074560 - (40) = \cdot92540$, and the denominator $= m + \cdot92540 + \alpha/m$. Whence VD (1) $= 29584 - 30726\alpha$. These give

$$\begin{aligned} \text{P}\,(1) &= 44693 - 25885 = 18808, \\ \text{S}\,(2) &= 25885 - 16566 = 9319, \\ \text{D}\,(1) &= 25885 - 29584 + 30726\alpha = -3699 + 30726\alpha. \end{aligned}$$

The P (1) or the first of the typical principal series would give $\lambda = 5316$. S (2) would be about $\lambda = 10731$. Neither have been observed. The S and D should be doublets with about $\nu = 1\cdot9$. The D line, $n = 3699$, is clearly the same as PASCHEN's 3719. If we make it so, α must be given by

$$30726\alpha = -20 + \text{error in D}\,(\,\infty\,),$$

or

$$\alpha = -\cdot000716 + \frac{\text{error in D}\,(\,\infty\,)}{30700}.$$

The error in D (∞) is probably considerable, which would make a small positive quantity. Not only is the deduced line close to the observed one, but the observed is a doublet of the proper amount. The doublet D (2) would be at $\lambda = 7651$, and has not been seen.

The foregoing is professedly speculative. If the relations found for the other elements really hold for Li, it shows that while in the others all the energy goes into vibrations of the positive type, in Li it goes into those of the negative type. It might be objected in the above, that there has been no evidence that the S and D forms, when used in a positive group of spectra, are different from the corresponding forms in a negative group. A similar difference will, however, be shown to exist when the spectrum of helium is considered. As we look down through the different elements we find traces of the negative type (VD−VF), (VD−VP). In Na the D series is not the ordinary but the F type, but we have seen indication of three lines of the typical form. In Li all the negative group come in, and we only have one indication of lines of the positive group. It is apparent, not that the formulæ have ceased to follow regular laws, but that the energy has passed from one set to another.

It is necessary to consider whether the identification of Paschen's doublet with the first line of the D series will hold if we regard the S and D forms to be the same for both positive and negative groups. The difficulty is, there is no appearance of the P form. It is possible, however, to determine VP (1) so as to make the identification correct, and see whether it leads to a likely value. Now

$$\mathrm{VD}\,(1) = 28580.$$

Hence

$$\mathrm{VP}\,(1) \sim 28580 = 3718,$$

or

$$\mathrm{VP}\,(1) = 32298 \text{ or } 24862,$$

giving values of the denominator of P respectively 1·8427 or 2·1003. The former is quite out of character, but the latter is more in character with analogy. It makes the D of P (1) only ·016 less than that of Na, and the fractional part greater than the $\mu - {\cdot}5$ of the S set, which for $m = 1$ is ·089. This fractional part is greater in all the previous cases. The identification, although possible, does not commend itself.

Hydrogen.

For our present purposes the spectrum of hydrogen is chiefly important, because on it is based the determination of the constant N. The value was determined by Rydberg on the supposition that Balmer's formula was correct, by applying the method of least squares to Ames'* measurements of the first 13 lines. I have already given reasons why, in deducing N, Rydberg's formula should be used in preference to Balmer's—the probability being that $\mu - 1$ would be so small that the term in α/m would be quite negligible. Also, since Ames' results, Evershed† has given measurements from solar prominences down to $m = 31$. For these reasons it seemed desirable to recalculate the value of N with Rydberg's formula. Rowland's measurements were used for HD (3.4). For HD (5) the readings of various observers differ greatly. The work was done twice—first for Ames' value of HD (5), weighting it one-half the others; and second, leaving out the line altogether. HD (6.7) have been very carefully and specially measured by Evershed‡. The remaining 24 lines used were from Evershed's measurements, all of course corrected to vacuo. In absence of any indication to the contrary, all observations were treated as of equal value, although as they are prismatic measurements it might have been better to

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[*] 'Phil. Mag.,' xxx., p. 33 (1890).

[†] 'Phil. Trans.,' vol. 197, p. 413.

[‡] 'Astro. Journ.,' xxviii., p. 72.

take wave-numbers as of equal value. It would, at any rate, have made the calculation simpler. The results are as follows:—

With AMES' HD (5)

$$n = 27419{\cdot}22-109708{\cdot}7/(m+{\cdot}000412)^2,$$

without

$$n = 27419{\cdot}21-109705{\cdot}8/(m+{\cdot}000374)^2.$$

The limits are practically the same. They are $109708{\cdot}7/(2{\cdot}000264)^2$. From the latter formula the values of obs.—calc. up to $m = 10$, and then at intervals of 5 to 30, and the last 31 are as follows:—

$m =$	3	4	5	6	7	8	9	10	15	20
	·01 R	−·07 R	·09 A	0	0	·03	·09	·04	−·17	·03
	25	30	31							
	−·03	−·20	−·14							

$m = 5$ is the doubtful measurement. In spite of the good agreement, however, the observations on which the determination of N is based are not at all as accurate as is desirable. PICKERING'S measurements of HS in ζ Puppis are far too inexact to give any information as to the value of N. The most accurately measured spectra are those of helium by RUNGE and PASCHEN, to which we next proceed. The HD and HF series should be almost identical, so that the observed lines should be close multiple lines, for which, as is well known, there is good evidence.

The combination principle in H has recently been illustrated by the discovery of two ultra-red lines by PASCHEN belonging to VP (3)—VD (m), $m = 4, 5$.

Helium.

The observations for the spectrum of helium are due to RUNGE and PASCHEN* for the visual and photographic region, PASCHEN† for the ultra red, and measurements of certain visual lines by interferential methods by Lord RAYLEIGH.‡ R. and P. estimate their possible errors to amounts of the order of ·005 A.U. There is no doubt but that their measurements give by far the most accurate values for any complete spectrum yet obtained, but the possible errors are certainly several times larger than their estimates. They estimated their possible errors for P′ (1) and P″ (1) to be respectively 80 and 48. PASCHEN'S later and very accurate determinations show that actually those errors were respectively 182 and 340. It is true that these were bolometric measurements, and naturally cannot be compared with the others, still

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* 'Astro. Journ.,' iii., p. 4.

† 'Ann. d. Phys.,' 27, p. 552 (1908).

‡ 'Phil. Mag.,' xv. (6), p. 548 (1908).

Rayleigh's interferential measurements allow us to compare some of these lines with what may be considered their actual values, and the comparison shows that the degree of accuracy is not nearly so high as that estimated by R. and P. The lines are given in the following list, together with the estimates of error by R. and P. :—

	Ray.	R. and P.	Est. err.	R.P. – Ray.
S″ (2)	7065·200	5·48	·030	·280
D′ (2)	6678·150	8·37	·005	·220
D″ (2)	5875·625	5·870	·006	·245
P′ (2)	5015·680	5·732	·007	·052
D′ (3)	4921·930	2·096	·013	·166
S″ (3)	4713·144	3·252	·014	·108
D″ (3)	4471·482	1·646	·005	·164

If R. and P.'s measurements are correct as a set they ought to show a constant ratio to the corresponding ones of Rayleigh, but a glance at the differences shows that this is by no means the case. With so large a number of lines for comparison as seven, it would seem legitimate to deduce what this ratio (k) should be for the whole of R. and P.'s scale, and thus to correct these seven at least. I have done this, making the mean square value of (correct-actual) least, treating first all observations as of equal value, and secondly as weighted according to R. and P.'s estimates. In both cases the result is the same, viz., $k = 1·000033$. If, as might possibly seem preferable, the ratio of difference to wave-length is to be a minimum, then $k = 1·000030$. On these suppositions we obtain the following corrections to apply to R. and P.'s lines to bring them into their true positions on their scale :—

I.		II.	
$d\lambda$.	dn.	$d\lambda$.	dn.
– ·045	+ ·072	– ·068	+ ·128
+ ·003	– ·006	– ·020	+ ·044
– ·049	+ ·147	– ·069	+ ·207
+ ·115	– ·460	+ ·100	– ·400
– ·002	+ ·008	– ·019	+ ·076
+ ·049	– ·245	+ ·033	– ·165
– ·015	+ ·075	– ·030	+ ·150

The List I.—actual errors a minimum—appears the better, in view of the fact that some of the corrections are within R. and P.'s estimates, and that they are generally smaller than in II. It would, perhaps, have been advisable to use these corrected values in determining N by least squares, but the work had been done before

Rayleigh's results were published. The work of applying the method to the six series is exceedingly laborious, and as the corrections themselves are not quite free from doubt, it did not seem worth while to recalculate. In any case, it is not probable that the actual values of N would be greatly altered. All six series have been treated in the same way, the observations being weighted in accordance with R. and P.'s estimates. In the case of the S series, however, the top line ($m = 2$) has been omitted. This was done because there is some doubt as to the correct form for the S formula, and any term β/m^2 has much less effect on the lower lines. Consequently the value of N is less likely to be affected. The resulting formulæ are :—

Singlet Series.

P′. . . . $32033{\cdot}094-109814{\cdot}6/(m+1{\cdot}014593-m^{-1}\times{\cdot}004392)^2$

S′. . . . $27174{\cdot}917-109726{\cdot}0/(m+{\cdot}861181-m^{-1}\times{\cdot}007809)^2$

D′. . . . $27174{\cdot}627-109672{\cdot}5/(m+{\cdot}996369+m^{-1}\times{\cdot}002917)^2$

Doublet Series.

P″ . . . $38453{\cdot}347-109666{\cdot}2/(m+{\cdot}929442+m^{-1}\times{\cdot}007792)^2$

S″ . . . $29222{\cdot}696-109719{\cdot}6/(m+{\cdot}705092-m^{-1}\times{\cdot}013408)^2$

D″ . . . $29222{\cdot}595-109689{\cdot}2/(m+{\cdot}996347+m^{-1}\times{\cdot}002200)^2$

The values of obs.—calc. are given in the following table, with the corresponding values from Ritz' formula, although they are not comparable on the same basis, except possibly in D′, P″, and D″, where the N is practically the old N, but Ritz gives no formula for the D series :—

m.	P′.			S′.			D′.		
	O.	H.	R.	O.	H.	R.	O.	H.	R.
1	·4	·096	– 80						
2	·007	– ·03	0	·05	2·95	0	·005	·545	
3	·003	·005	0	·007	·002	0	·013	·000	
4	·002	·002	0	·005	·001	·046	·004	·000	
5	·004	·021	– ·001	·007	·000	0	·006	·000	
6	·005	·000	– ·038	·006	·005	– ·033	·003	·005	
7	·008	·028	– ·032	·011	– ·060	– ·087	·005	– ·024	
8	·005	– ·028	– ·116	·009	·010	– ·022	·010	·009	
9	·004	– ·025	– ·13	·014	·000	– ·060	·011	·007	
10	·011	– ·020	– ·12		– ·022		·007	·000	
11		·000	– ·09		·08	·000	·007	·012	
12	not	observed.			– ·207	– ·285		·016	
13		·27	·08					– ·020	

m.	P″.			S″.			D″.		
	O.	H.	R.	O.	H.	R.	O.	H.	R.
1	·15	·80	0						
2	·004	·046	0	·030	2·84	0	·006	·005	
3	·010	– ·018	– ·056	·014	– ·026	0	·005	·006	
4	·004	·016	0	·003	·007	·036	·003	·003	
5	·006	– ·004	– ·007	·002	– ·004	0	·002	– ·005	
6	·013	·002	– ·003	·004	– ·002	– ·016	·002	·002	
7	·010	– ·012	– ·013	·004	– ·006	– ·035	·003	·005	
8	·013	·013	– ·083	·005	·020	·035	·004	·006	
9	?	– ·024	– ·013	·007	·007	·003	·014	·028	
10	?	– ·080	– ·019	·01	·014	– ·037	·015	·002	
11	?	·151*		·02	·030	·000	·016	– ·017	
12	?	– ·014*		·02	– ·051	– ·073	·02	·021	
13				·02	– ·055	– ·060	·016	– ·007	
14				?	·107	·040	·016	– ·017	
15							·02	– ·049	
16							·02	– ·047	
17							?	·24	
18							?	– ·10	

* SCHNEIDERJOST, 'Beiblätter,' xxviii., p. 1175.

The agreement between observed and calculated is very good except for S′(2) and S″(2), which is in accordance with what has been found in the previous cases. As mentioned above, these were left out in finding the constants, as the chief end was to get accurate values of N, and there was some doubt as to the form of the S formulæ being correct. In comparison of RAYLEIGH'S lines we found probable errors in R. and P.'s measurements, amounting to eight or ten times their estimates. If we take their possible errors as only three times their estimates, very few of the calculated values overstep these limits. It is interesting to note that the least square treatment corroborates independently the errors determined from RAYLEIGH'S interference standards. Thus, in P′(2), the differences in *n* for $m = 1.2.3.4$ are $-·024$, $+·12$, $-·03$, $-·03$, pointing to considerable error in P′(2). If the calculated correction of II. be applied to R. and P., the difference should have been $-·28$. This would have been in the course $-·024$, $-·28$, $-·03$, and then the method of least squares would have brought these into close agreement. In fact, the considerable error in P′(2) has pulled the calculated values for P′(1.3.4) out of their proper places. A similar result is shown in S″. If the calculated wave-length values of S(2.3) be compared with R. and P.'s corrected values from II., the differences would be 2·75, ·007, ·007, instead of 2·84, $-·026$, ·007, and if they had been used to calculate the constants the agreement would have been much closer. So the differences for D(2) would be diminished from ·545 to ·525, but D(3) increased from 0 to $-·019$, D(2.3) increased from ·005, ·006 to $-·064$, $-·024$.

The values of N may be expected to depend to a few units on the weights allowed, and the accuracy of the measurements. Allowing for this, the evidence, with one exception, bears out what we have already had reason to infer, viz., that the P and D series have about the same value of N, and that that of S is larger. The exception is P′. The mean of N of D′, P″, D″ is 109675·9, or practically RYDBERG'S old value obtained from H. We may feel, therefore, reasonable certainty that the actual value for these series is very close to 109675. The N for the two S series are again practically the same about 109725, but there is some uncertainty owing to the top lines having been omitted. The case of P′ is exceptional with the large value of 109815. The agreement of the calculated with the observed values is not so good as in the other cases. It must be left at present as an apparent anomaly, but it may be noted that P′ is a singlet series, like that of Li, in which a similar case arises. In the alkalies we saw that N for S increased with atomic weight, and if this were the general rule we ought not to expect a large value of N for helium. For this reason He is not a good test. We shall find better ones when we come to deal with other spectra.

It is seen that the limits of the S and D series for both sets are very closely the same. Also VP′(1) = 27175·73 and S′(∞) = 27174·627, whilst VP″(1) = 29221·89 and S″(∞) = 29222·696, so that, as in the other elements, relation (F) is very closely verified. On the other hand again, as in the other cases, relation (G) is only roughly satisfied. VS′(1) = 31943·65, VS″(1) = 38339·45, which differ from P′(∞) and P″(∞) by 89·44 and 113·9 respectively.

The two D series run nearly parallel to one another. The differences of corresponding wave-numbers are 2044·48, 2045·99, 2046·93, 2047·37, 2047·55, 2047·48, 2047·77, 2047·60, 2047·81, 2048·06, 2048·17, 2047·79. The two series run down to limits which will be very close to the true values for the last six lines, which give a mean of 2047·86. Taking this, the values of VD(m) for the two series differ by numbers which are given in the first row of the table below. The denominators of VD are $m+\cdot996\ldots+\ldots$ or $m+1$ roughly. There are three cases to consider as to the origin of these differences: (1) an alteration in N, the differences will then be $\delta\mathrm{N}/(m+1)^2$; (2) an alteration in μ, when the differences will be $2\mathrm{N}\,\delta\mu/(m+1)^3$; (3) an alteration in α, when they will be $2\mathrm{N}\,\delta\alpha/(m+1)^4$. The second, third, and fourth rows give the numerical differences in each of these cases, the first difference being that observed, viz., 3·38. The fifth row gives the result of dividing successive differences by 2—in other words, making the difference depend on a term $\mathrm{A}2^{-m}$.

	2.	3.	4.	5.	6.	7.	8.	9.	10.	11.	12.	13
I. . .	3·38	1·87	·93	·59	·31	·38	·09	·27	·05	−·20	−·31	·07
II. . .	3·38	1·90	1·21	·84	·62	·47	·37					
III. . .	3·38	1·42	·73	·42	·27	·18	·12					
IV. . .	3·38	1·07	·44									
V. . .	3·38	1·69	·84	·42	·21	·10	·05					
VI. . .	4·58	1·84	·92	·53	·33	·21	·11	·09	·04	·02		

The difference for $m = 7$ in I. is clearly wrong, the mean of 6 and 8 gives ·20, so also is that for $m = 9$, and beyond this the measurement errors are clearly greater than the differences themselves. It will be seen by inspection that a change in N alone gives too slow a decrease and a change in α alone too quick. A change in μ gives about the correct average descent with increasing m, but $m = 3, 4$ are too much out to be due to mere errors of observation. Row V., term in $A/2^{-m}$, marches closely with I. On the other hand, VI. is extremely close. It gives the differences as calculated from the formulæ obtained by least squares, which has met the difficulty by increasing N by 17 and diminishing the denominator by $\cdot 000022 + \frac{\cdot 000717}{m}$. Now $\cdot 0141 w^2$ for He is ·000022, which is evidence that we have here to do with the regular atomic weight term.

So far nothing has been said as to the true form of the series, but the usual classification has been followed. With our present knowledge, however, a glance at once shows that the third series in each set belongs to the F sequence, and that the sets of series should be classified as follows:—

$$\text{Singlet series positive type}\left\{\begin{array}{l}\text{VS}'(1)-\text{VP}(m)\\ \text{VP}(1)-\text{VS}'(m)\\ \text{VP}(1)-\text{VF}(m)\end{array}\right. \qquad \text{Doublet series negative type}\left\{\begin{array}{l}\text{VS}''(1)-\text{VD}(m)\\ \text{VD}(1)-\text{VS}''(m)\\ \text{VD}(1)-\text{VF}(m)\end{array}\right.$$

The sets are apparently independent, except as depending on the same He fundamental sequences. In the singlet series the negative type is wanting; in the doublet the positive is wanting. They are, as is well known, developed in different ways, and it is not to be expected that the P sequence of the first is also that of the second, and the D sequence of the second the same as that of the first. The singlet series stands out by itself also as having a much larger value of N for the P sequence than in any of the other spectra. In the doublet series, however, it might be expected that similar relations to those found in the other elements might exist. For instance, the D of VF(1) is ·998547. The μ of VD is ·9294 or ·0691 (say ·0700) less. If this depends on the atomic volume constitution of the term, as indicated in the alkalies, it should be possible to determine the atomic volume of solid He by comparison with any of the alkali spectra. Now K, with an atomic volume of 44·617, gives for the corresponding difference about ·300. On this supposition, therefore, the atomic volume of He would be 10·41. The density of solid He should, therefore, be ·38. KAMERLINGH ONNES gives that of liquid He at its condensing point as ·154. The density of the solid would probably be considerably greater, but scarcely so large as ·38. The deduction, of course, is not reliable, but is interesting as deducing a value of the right order of magnitude. It may be noticed that the μ of S′ differs from that of S″ by $\cdot 1560 = 2 \times \cdot 0780$; μ of P′$-\mu$ of S′ by $\cdot 1534 = 2 \times \cdot 0767$; and μ of D″$-\mu$ of S″ by $\cdot 2243 = 3 \times \cdot 0748$, all approximately multiples of the ·075 which go to build up the alkali series. Whether this has any real significance, however, must be at present an open question.

Further Discussion.

From the foregoing discussion a few points stand out for further consideration. The most important is the doubt as to the form for the S series.

The dissatisfaction with the form in α/m for the S series arises from the fact that VS (1) does not give P (∞), and that in some cases the value of S (2) calculated by it from constants determined from S (3.4.5) is considerably outside the limits of observation, certainly in the case of K, and probably also for Rb and Cs. This second failure, however, clearly is a consequence of the first, and will probably be corrected if the first is. In addition, the $\mu - \cdot 5$ of the S is so close to the value of the atomic volume term in P as to point to a real equality if the true form be obtained, whilst the value of α in S is always considerably less than that in P. It has been shown that the VS (1) cannot be made = P (∞) without introducing a term in β/m^2, and that in the two numerical examples given for Na and K, the α and β come about equal—in other words, a denominator $= m+\mu-\alpha m^{-1}(1+m^{-1})$ would satisfy all the conditions. Also the $\mu - \cdot 5$ is brought nearer to the atomic volume term, but α becomes about one-half that in the P series. Before considering this clue further, two other ways out of the difficulty may be mentioned. Ritz has systematically used $m + \cdot 5$ in place of m in the S series. But the adoption of $\alpha/(m+\cdot 5)$ in place of α/m makes the disagreement between VS (1) and P (∞) greater, although it brings the α more into agreement with that of P. On the other hand, $m - \cdot 5$, which makes the μ of S in the alkalies practically the same as that in P, throws the difference the other way. It is clear, then, that since m = integer makes VS (1) < P (∞), and $m - \cdot 5$ makes VS (1) > P (∞), that a value of $f < \cdot 5$ can be found, such that a denominator $= m + \mu - \dfrac{\alpha}{m-f}$ would make the limits come correctly.

In all that precedes, not only has the value of N been taken to be a universal constant, but it has had the special value 109675 attached to it. The evidence for the universality of its value is not, however, conclusive, and it is clearly possible, if it be not so, to assign values N_p, N_s to N, so that

$$N_p/D^2 \text{ of P (1)} = \text{S} (\infty), \qquad N_s/D^2 \text{ of S (1)} = \text{P} (\infty),$$

and such contingency at least requires examination. These three possible solutions will now be taken in order.

Addition of Term in β/m^2.—We have seen that it is possible to satisfy the required conditions in the case of Na and K, but only by allowing actual errors in the measurements alternately positive and negative, and each a considerable fraction of the possible. The necessity of taking in each case the errors alternately positive and negative makes this way out of the difficulty very doubtful, and any one using Kayser and Runge's observations gets to doubt whether many of their actual errors are more than small fractions of the possible. It would probably be possible to satisfy the conditions for Rb and Cs within the present possible errors, but only because they are so considerable. I think, therefore, on the whole, the evidence is against this explanation. As, however, the coefficients α and β were nearly the same in the numerical examples, this point was tested for Na, using P (1) for −S (1), Paschen's S (2), and K. and R.'s S (3). The resulting formula was

$$n = 24477{\cdot}04 - \mathrm{N}\Big/\left[m - {\cdot}651450 - {\cdot}012403\left(\frac{1}{m} + \frac{1}{m^2}\right)\right];$$

but the deviations for the other lines were far too great, being several times the possible.

Term $\alpha/(m-f)$.—The value of f, as determined from the observations, will depend so much on the exactness of the measures of P (1.2) and S (2.3) that we can expect to learn nothing from considering the cases of Rb and Cs. For Na and K the resulting formulæ are

For Na

$$\mathrm{P} \quad . \quad . \quad 41445{\cdot}27 - \mathrm{N}\Big/\left(m + 1{\cdot}150156 - \frac{{\cdot}035510}{m + {\cdot}070}\right)^2,$$

$$\mathrm{S} \quad . \quad . \quad 24472{\cdot}46 - \mathrm{N}\Big/\left(m + {\cdot}655055 - \frac{{\cdot}022786}{m - {\cdot}192}\right)^2,$$

and for K

$$\mathrm{P} \quad . \quad . \quad 35000{\cdot}53 - \mathrm{N}\Big/\left(m + 1{\cdot}302556 - \frac{{\cdot}078531}{m + {\cdot}1557}\right)^2,$$

$$\mathrm{S} \quad . \quad . \quad 21963{\cdot}75 - \mathrm{N}\Big/\left(m + {\cdot}824259 - \frac{{\cdot}039382}{m - {\cdot}2718}\right)^2.$$

These give values of obs. − calc. as follows:—

	1.	2.	3.	4.	5.	6.	7.
NaP . .	0	0	0	0	−·03	**−·15**	
NaS . .		**1·27**	0	0	0	**·42**	
KP . .	0	0	0	**−·15**	**−·10**	**−·33**	
KS . .		**9·45**	0	0	0	·05	·18

By comparison with Table I., it will be seen that now NaP (6) comes outside the limits, NaS (2) is slightly better (but can be brought inside as before). KP_1 is much worse, and KS (2) improved, but the relation between the limits now holds. No relationships are apparent between the various constants, except that, allowance being made for possible variations, the f of P in both cases is one-half $\mu - 1$. The inequality between the α for the P and S series is increased.

N *not constant.*—In this case the values of N are supposed to be different for both the P and S series. Each series, therefore, requires as before three lines to determine its constants, and the relations $P(\infty) = VS(1)$ and $S(\infty) = VP(1)$ give two additional equations to determine the two values of N—say, N_p and N_s. Unfortunately the values of the first lines are so uncertain (with exception of NaP(1)) that the values of N_p-N and N_s-N vary very largely with the errors in the observed lines. For instance, in the case of Rb, if L.'s values for P(1) and S(3) be used, $N_p-N = -12$, $N_s-N = 1300$. If S.'s values for P(1) and S(3.4) are used, $N_p-N = 141$, $N_s-N = 651$. In the first case P is reproduced as well as the original, but S not so well; in fact, $S(\infty)$ comes out too large. In the second, P is not so good, and S is better than with the 1300 difference. The discussion shows, however, that within easy limits of error the N of P may be taken as constant, and for a provisional value the usual value of N will do very well.

For Na, using K.R.'s values for S(3.4.5), $\delta N_s = 215$, $\mu = \cdot661089$, $\alpha = -\cdot032760$, and the calculated lines for S agree better than the original except, however, S(2), which is $-4\cdot28$ wrong in place of $1\cdot37$. If, however, PASCHEN'S S(2) is used and K.R.'s S(3.4), then $\delta N_p = 306$, $\delta N_s = 588$, the limits are considerably altered, and the calculated results bad. If we make $\delta N_p = 0$ and use PASCHEN'S S(2) and K.R.'s S(3), $\delta N_s = 342$, and the other calculated lines are all outside the limits. The most reliable result appears, therefore, to be that calculated from K.R.'s values for S(3.4.5), which improves all the other lines but requires S(2) to be 4·28 A.U. larger than PASCHEN'S observation, which can hardly be the case.

For K, using K.R.'s S(3.4.5), $\delta N_s = 609$, $\mu = \cdot841460$, $\alpha = -\cdot066494$. This brings S(2) within ·22 of PASCHEN'S value (original difference $-16\cdot20$), and all the others within limits.

For Rb, using S.'s values for S(3.4) and K.R.'s for S(5), gives $\delta N_p = 141$, $\delta N_s = 651$, $\mu = \cdot894830$, $\alpha = -\cdot085235$, but the P series is bad, although S is better than that referred to above where $\delta N_s = 1300$. It is probable that a value between 651 and 1300 would be preferable.

For Cs, using L.'s for P(1), K.R.'s for P(2.3), and S.'s for S(3.4.5), gives $\delta N_p = 369$, $\delta N_s = 1286$, $\mu_p = 1\cdot458065$, $\alpha_p = -\cdot092888$, $\mu_s = \cdot992400$, $\alpha_s = -\cdot112079$. These bring all the lines within limits, P better than the ordinary.

It is to be noticed that although N_p may be kept constant by giving permissible variations to the lines from which the constants are determined, yet there is a tendency shown to an increase with increasing atomic weight. In all cases N_s increases with increasing atomic weight, but the calculated values vary so much with the actual errors of observation, that it is useless to attempt to find any relation between them. δN_s for Na is probably not far from 220; for the others it is larger. The values of δN_s for K, Rb, Cs *might* be the same, but in view of the smaller value required for Na, this is not likely. One important fact brought out, however, is the raising the value of α for S, so that its ratio to $\mu-\cdot5$ becomes much closer to that for the P series.

If the condition that α/μ should be the same as for P be applied, say about ·2, the values of δN_s come to about 382 for Na and 650 for the others.

In the present state of the observations, it is useless to attempt to arrive at anything more definite than that a very small proportionate increase of N for the S series will satisfy relations (F and G), make better agreement in general for the lines S (2), and bring the ratio $\alpha/(\mu-\cdot 5)$ into close agreement with that for P. Possibly some constant value for δN_s would make α the same as for the P series, in which case the μ of S would be formed, not by adding the term *sb* to ·5, but to a number $>\cdot 5$. For these combined reasons it would appear, so far as our knowledge at present extends, that the required improvement in the S formulæ should be looked for in a change of the value of N. The evidence shows that at least the greater part of δN_s does not depend, like W, on the square of the atomic weight. It might, however, depend on *s*. Thus apparently δN for NaS is about 300, for KS about 600, and the corresponding multiple law would make it 750 for Rb and 900 for Cs, quite in agreement with the actual numbers found. If this were so, the P sequence would be formed by adding a multiple term to the denominator, and the S sequence by adding a corresponding multiple term to the numerator.

A further argument in support of this theory is found from the discussion on the various He series. It was there found that using least squares to these very accurately measured spectra, rich in lines, that the F and D sequences have values of N very close to the value 109675 generally adopted, but that the S series in both cases require a value of N about 50 larger, and this when the lines corresponding to $m = 2$ were not used. In this case they do not reproduce the values of S (2). It is probable, therefore, that if they were introduced the values of N would be still more considerably increased. The case of HeP′ requires a still higher value of N, and in this case HeP′ (1) agrees with the observed. It seems a clear case for an increased N if the form $m+\mu+\alpha/m$ is absolute. The argument that it is so is that in cases of elements where μ and α are comparatively large, it is sufficient to give practically all the lines within limits of observation errors, and that if β/m^2 be added, β comes always a small fraction of α and capable of being wiped out by errors of observation. Now the α in the He spectra are all very small, and β would be very much smaller, and exert scarcely any influence on the lines beyond the first two or three. Nevertheless N is increased for the S sequences.

Summary of Results.

The principal results arrived at in the foregoing discussion may be summarised as follows :—

1. A modified RYDBERG's formula, in which the denominator is of the form $m+\mu+\alpha/m$, is found to be capable of representing practically all the observed lines

within errors of observation. The chief exception is for the first line of the sharp series, which is shown to be probably due, on other evidence, to a change in N.

2. The existence of a new fundamental sequence F (m) whose denominator is either $m+\mu-2\mathrm{W}$ (RITZ) or $m+\mu-2\mathrm{W}\left(1-\frac{1}{m}\right)$, where W, the atomic weight term, is a small fraction of the square of the atomic weight. The dependence of the fraction on the element is not at present determined, but if w denote the atomic weight divided by 100, the fraction of w^2 is ·0141 for Na and about $s/(s-1)\times$ ·0141 for the others.

3. That the D of the P sequence is found by adding $\cdot 074560\left(1-\frac{\cdot 21521}{m}\right)s$ to $1-\mathrm{W}\left(1-\frac{1}{m}\right)$, as found from the F sequence, where s has the values 2.4.5.6 for Na, K, Rb, Cs. In the case of Cs, however, in which satellites appear in the D series, the term in $\mathrm{W}\left(1-\frac{1}{m}\right)$ does not occur.

4. The D of the P_2 sequence is found by deducting 2W, or approximately $\cdot 0141w^2\left[1+\frac{1}{m(s-1)}\right]$, from that of P_1.

5. The μ of the D sequence is found by deducting the same quantity $\cdot 074560s$ from $1-\mathrm{W}(1-m^{-1})$. The form of the term in α has not been determined. When, however, satellites occur, and there are two D sequences, as in Cs, the W missing in the P sequence must be put in here, and the above quantity $\cdot 074560\times 6$ deducted from $1-2\mathrm{W}$ instead of from $1-\mathrm{W}$. This gives the μ for D_{21} or D_{12}. The μ of $D_{11}(2)$ is found by adding $\frac{1}{2}\mathrm{W}$ to that for D_{12}, *i.e.*, $\mathrm{W}(1-m^{-1})$.

6. In the same way as the P sequence forms a doublet D series, $\mathrm{VP}_1(1)-\mathrm{VD}(m)$, $\mathrm{VP}_2(1)-\mathrm{VD}m$, so do the D sequence produce a F series—doublet when D has satellites—viz., $\mathrm{VD}_{11}(2)-\mathrm{F}(m)$, $\mathrm{VD}_{12}(2)-\mathrm{F}(m)$.

7. The values for the S series show that its μ is obtained by deducting quantities somewhat smaller than ·5 from that for the P, and that its α is always considerably less than that of P. Also, although RYDBERG's relation $\mathrm{S}(\infty)=\mathrm{VP}(1)$ is very closely verified, the other, $\mathrm{P}(\infty)=\mathrm{VS}(1)$ cannot be true with the formulæ used. Moreover, the formulæ fail to reproduce S (2) within limits of error. Evidence is given that this is due to a change in value of N in the S sequence. A suitable change makes $\mathrm{P}(\infty)=\mathrm{VS}(1)$, the difference of the μ of S and P the same for each element, α the same for S and P, and the values of S (2) within the limits. Moreover, in using the He spectra to obtain a more exact value of N than can be expected from H, it is found that N is greater than 109675 for S, by about the same amount in both the singlet and doublet series, whilst close to it for the D′, D″, and P″. The evidence in favour of this explanation is therefore very strong, and the D of S would then be found by subtracting $\cdot 5-x$, where x is small of order ·1 from that of P.

8. The spectrum of Li is abnormal. It is a singlet series in which what has been

called the Principal series is formed on the D sequence, and what has been called the D on the F sequence. The set belongs to what has been here called the negative type. The first, the so-called Principal, is the only one in which the formula does not reproduce all the lines. It is possible that it requires a larger N, as is required for the P lines in the other singlet series discussed, viz., He′.

9. As we pass down through the alkali metals we find a change of type occurring, first in Na, and then in Li. In Na, what is called the D series, has a μ much closer to the F type than to the D type. There seems to be a certain instability, and a large number of extra lines appear whose development appears to depend on narrow limits of temperature, amongst these are possibly three lines which show the D type normal to the other elements. In Li all the normal type have disappeared, and we get a singlet system depending on a new kind of D sequence for the Principal series, and the F sequence for the D series. In addition, we get lines conforming to the D type based on the new D sequence. Also there are indications of the normal D series in a doublet spectrum, with the doublet separation to be expected in the normal type. But no P or S lines of the normal type have been seen.

10. In He the singlet sets of series are of the P type, with the associated D based on the F sequence. The doublet sets are of the D type with the associated D also based on the F type. These spectra have been used to determine accurate values of N by the method of least squares. The important result comes out that the value of N is not the same for each series. It is practically 109675 for the D′, D″, and P″ sets, 109725 for S′ and S″ (probably higher if the lines S (2) had been employed in the determination), and 109810 for P′.

The relations found strengthen the evidence in favour of Lord RAYLEIGH's theory as to the kinematical origin of these spectra. A general consideration of questions relating to origin is, however, postponed until the spectra of the other elements are discussed in a future communication.