XXIV.—On the Structure of the Series of Line- and Band-Spectra. By J. Halm,
Ph.D., Lecturer on Astronomy in the University of Edinburgh.

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In a preliminary note read before the Society on July 4, 1904, I drew attention to the fact that a number of line-series, forming a group which includes the first series of Hydrogen, can be represented by an equation of the form

$$\frac{1}{\nu_{\infty} - \nu} = a_1 m^2 + b_1, \quad (1)$$

where ν denotes the wave-frequency of any line of the series, ν_{∞} that of the so-called "tail" of the series ($m = \infty$), and a_1 , b_1 constants depending on the nature of the emitting substance; the frequencies of successive lines being obtained by substituting successive integers for m . We see at once that this equation is a generalisation of BALMER'S formula, into which it is transformed by equating b_1 to zero. In the same note I also pointed out the existence of another group represented by an equation of the same form, if $(m + \frac{1}{2})$ is substituted for m . As a special case ($b_1 = 0$) this group contains the second Hydrogen series discovered by Professor PICKERING in the spectrum of ζ Puppis. Subsequent investigations convinced me, however, that, although a considerable number of line-series may be classified into these two groups, there are numerous instances where the more general formula

$$\frac{1}{\nu_{\infty} - \nu} = a_1(m + \mu)^2 + b_1 \quad (2)$$

must be employed, in which μ represents various fractional numbers. Also, in studying more thoroughly the literature on the subject, I found that the equation, in the last-mentioned form, is merely a modification of a mathematical expression already employed by Professor THIELE in his investigations on the band-series of the carbon spectrum and on the line-series of Helium. But, convinced as I was from my own computations of the accuracy and general importance of this equation, I was surprised to find it rejected by Professor THIELE, on the ground that it did not sufficiently represent the observed wave-lengths. This statement appeared to be so far from acceptable, that I resolved to demonstrate, by an exhaustive examination of all the known series, not only the general applicability of equation (2), but also its great superiority over any other formula hitherto proposed. The demonstration of this fact will be the first object of the present communication. It will be shown that the equation represents not only all the line-series hitherto known, but also the band-series, with an accuracy which leaves nothing to be desired. But far more important even than the demonstration of equation (2) as an empirical formula of practical usefulness are certain conclusions which may be drawn from the character of this equation and the numerical values of its constants. For instance, we shall see that equation (2) can be represented

in a geometrical form, by means of which we are enabled to collect all the line- and band-series into one single diagram revealing a community of properties between the two classes of spectral regularities and their individual members. This new geometrical connection between the series appears to be of theoretical importance, inasmuch as it shows a striking similarity between the vibrations of a radiating system of atoms and the nodal vibrations of elastic bodies. From this point of view an important relation has been discovered between the wave-frequencies of the "tails" of line-series and the atomic volumes of the emitting elements. In the course of this paper we shall have frequent opportunities of observing regularities in the constants of equation (2), and of drawing from them conclusions which cannot but be of some importance, however small, in connection with the theory of the phenomena of spectral regularities—a region into which the speculative mind has so far vainly attempted to penetrate. The outcome of the investigation must, I think, be to convey the impression that equation (2) is to be considered as more than a merely empirical formula, and that, if it does not represent the physical law itself, it is at least a remarkably close approximation to it, sufficiently reliable, perhaps, to guide the theorist in his search for the ultimate cause of the spectral regularities here considered.

Before entering upon the first part of our investigation, viz. that dealing with the question how far equation (2) is capable of representing the observed wave-frequencies, it will be useful to derive other forms of this equation, which we shall employ later on. First of all, we see at once that (2) may be expressed by the following series :

$$\nu = \nu_\infty - \frac{1}{a_1(m+\mu)^2} - \frac{b_1}{a_1^2(m+\mu)^4} - \frac{b_1^2}{a_1^3(m+\mu)^6} + \dots$$

and we notice that in this form it represents a more general case of RYDBERG's formula, into which it converges, for $b_1 = 0$. In order to express the fact of its belonging to this type, and at the same time to distinguish it from RYDBERG's more special equation, I propose for it the name "RYDBERG-THIELE" equation, recognising thereby Professor THIELE's merit in having first introduced its present form into spectroscopic science. Equation (2) assumes a simpler and in some cases a more convenient form by introducing ν_0 , the wave-frequency corresponding to $m + \mu = 0$. In most cases there is no line referring to this special value of ν , which obviously must lie close to the "head" of the series. But for the sake of convenience we may be permitted to speak of ν_0 in the following formulæ as the wave-frequency of the "beginning" of the series. Introducing ν_0 , we find from (2) :

$$\frac{\nu - \nu_0}{\nu_\infty - \nu} = a_1(\nu_\infty - \nu_0) \cdot (m + \mu)^2 = a_2(m + \mu)^2. \quad (3)$$

Similar equations are at once obtained if wave-lengths are substituted for wave-frequencies :

$$\begin{aligned} \frac{1}{\lambda - \lambda_\infty} &= \frac{a_1}{\lambda_0^2} (m + \mu)^2 + \frac{1}{\lambda_0 - \lambda_\infty} = a_1(m + \mu)^2 + \beta_1 \\ \frac{\lambda_0 - \lambda}{\lambda - \lambda_\infty} &= a_1 \frac{\lambda_0 - \lambda_\infty}{\lambda_0^2} (m + \mu)^2 = a_2(m + \mu)^2 \end{aligned} \quad (4)$$

Still more convenient for computation are the following transformations, in which ν_x and λ_x , the wave-frequency and wave-length of the x th line of the spectrum, are introduced :

$$\begin{aligned}\frac{1}{\nu - \nu_x} &= \left(\frac{1}{\nu_\infty - \nu_x} \right)^2 \cdot \frac{1}{a_1} \cdot \frac{1}{(m + \mu)^2 - (x + \mu)^2} + \frac{1}{\nu_x - \nu_x} = \frac{a_2}{(m + \mu)^2 - (x + \mu)^2} + b_2; \\ \frac{1}{\lambda_x - \lambda} &= \left(\frac{\lambda_x}{\lambda_0 - \lambda_\infty} \right)^2 \cdot \frac{1}{a_1} \cdot \frac{1}{(m + \mu)^2 - (x + \mu)^2} + \frac{1}{\lambda_x - \lambda_x} = \frac{a_3}{(m + \mu)^2 - (x + \mu)^2} + \beta_3.\end{aligned}\quad (5)$$

The advantage of using these two formulæ lies in the fact that we may choose for ν_x or λ_x the wave-frequency or wave-length of any *observed* line of the series, whereas in the preceding equations ν_0 , ν_∞ and λ_0 , λ_∞ are quantities not directly obtainable from the observations. The arithmetical process of evaluating the other three unknowns is thereby greatly facilitated. Lastly, we may write

$$\begin{aligned}\frac{1}{\nu - \nu_0} &= \frac{1}{a_1(\nu_\infty - \nu_0)^2(m + \mu)^2} + \frac{1}{\nu_x - \nu_0} = \frac{a_4}{(m + \mu)^2} + b_1; \\ \frac{1}{\lambda_0 - \lambda} &= \frac{1}{a_1} \left(\frac{\lambda_x}{\lambda_0 - \lambda_\infty} \right)^2 \cdot \frac{1}{(m + \mu)^2} + \frac{1}{\lambda_0 - \lambda_\infty} = \frac{a_4}{(m + \mu)^2} + \beta_1.\end{aligned}\quad (6)$$

equations which will be specially useful in the investigation of the band-series.

In comparing first our formula with the observed wave-frequencies of line-series, we shall make use of equation (2), and apply it in this form to all the series mentioned in Professor KAYSER's *Handbuch der Spectroscopie*, vol. ii. I may state at once that in all cases the constant μ was found to be a proper fraction, the denominator of which is represented by an entire multiple of 5, or, expressed in algebraic symbols, $\mu = \frac{p}{5q}$, p and q being integers. As unit of wave-length the tenth-metre or Angström unit was adopted, while for ν the value $10^8\lambda^{-1}$ was taken, in accordance with KAYSER and RUNGE and others. When not mentioned otherwise, the wave-lengths and oscillation-frequencies are reduced to the Rowland scale.

A. LINE-SERIES.

Group of Alkali metals.—There are two distinct kinds of series of spectra in the elements of this group: the “principal” series, consisting of strong and sharply defined lines—the principal lines of the spectrum—which are easily reversible, and one or two fainter “subsidiary” series represented by hazy lines, with little or no tendency to reversal. These lines have been observed with very different degrees of accuracy. KAYSER's tables contain a column indicating the estimated probable limits of the observational errors expressed in units of wave-length. These limits are given in the last columns of the following tables, but in units of wave-frequency. Although the estimated uncertainties of the observed wave-lengths cannot be considered as quite reliable, they may nevertheless convey an approximate idea of the accuracy to be expected in our comparison.

1. Lithium.

PRINCIPAL SERIES.

$$\log a_1 = 4.95920 - 10 \quad \nu_\infty = 43498.5$$

$$\log b_1 = 3.55776 - 10$$

$(m + \mu)$	ν obs.	ν comp.	Obs. - Comp.	Limits of Error of Obs.
1.95	14907.1	14907.0	+0.1	0.4
2.95	30933.2	30932.8	+0.4	0.3
3.95	36477.8	36475.7	+2.1	0.4
4.95	39022.9	39022.5	+0.4	0.5
5.95	40401.9	40399.1	+2.8	1.7
6.95	41227.8	41226.0	+1.8	1.8
7.95	41761.7	41761.5	+0.2	3.5
8.95	42124.8	42127.7	-2.9	?
9.95	42383.7	42389.2	-5.5	?

1. SUBSIDIARY SERIES.

$$\log a_1 = 4.95899 - 10 \quad \nu_\infty = 28594.7$$

$$\log b_1 = -\infty$$

$(m + \mu)$	ν obs.	ν comp.	Obs. - Comp.	Limits of Error of Obs.
3.0	16383.3	16383.3	0.0	0.1
4.0	21727.9	21725.7	+2.2	0.5
5.0	24198.8	24198.6	+0.2	1.2
6.0	25541.5	25541.8	-0.3	1.3
7.0	26351.2	26351.8	-0.6	34.5
8.0	26889.7	26877.5	+12.2	36.5
9.0	27243.5	27237.9	+5.6	38.0

2. SUBSIDIARY SERIES.

$$\log a_1 = 4.96060 - 10 \quad \nu_\infty = 28583.3$$

$$\log b_1 = 3.48865 - 10$$

$(m + \mu)$	ν obs.	ν comp.	Obs. - Comp.	Limits of Error of Obs.
2.6	12304.0	12304.0	0.0	?
3.6	20112.2	20112.2	0.0	0.4
4.6	23400.4	23400.3	+0.1	1.1
5.6	25088.2	25087.9	+0.3	1.2
6.6	26053.2	26067.5	-14.3	21.0

2. Sodium.

PRINCIPAL SERIES (1st Component).

$$\log a_1 = 4.95369 - 10 \quad \nu_\infty = 41467.8$$

$$\log b_1 = 4.43154 - 10$$

$(m + \mu)$	ν obs.	ν comp.	Obs. - Comp.	Limits of Error of Obs.
2.2	16960.2	16960.2	0.0	...
3.2	30274.9	30274.9	0.0	0.3
4.2	35051.9	35051.7	+0.2	0.6
5.2	37307.0	37307.2	-0.2	1.3
6.2	38550.8	38550.9	-0.1	1.5
7.2	39310.5	39309.2	+1.3	1.5
8.2	39805.3	39804.8	+0.5	3.2

1. SUBSIDIARY SERIES (1st Component).

$$\log a_1 = 4.95740 - 10 \quad \nu_\infty = 24481.2$$

$$\log b_1 = 3.16660 - 10$$

$(m + \mu)$	ν obs.	ν comp.	Obs. - Comp.	Limits of Error of Obs.
3.0	12202.9	12202.9	0.0	?
4.0	17580.1	17580.2	-0.1	0.5
5.0	20066.1	20066.1	0.0	0.8
6.0	21416.0	21415.7	+0.3	2.2
7.0	22222.2	22229.3	-7.1	4.9
8.0	22759.9	22757.2	+2.7	?
9.0	23117.7	23119.2	-1.5	?

2. SUBSIDIARY SERIES (1st Component).

$$\log a_1 = 4.95369 - 10 \quad \nu_\infty = 24490.4$$

$$\log b_1 = 4.29709 - 10$$

$(m + \mu)$	ν obs.	ν comp.	Obs. - Comp.	Limits of Error of Obs.
3.7	16230.7	16230.8	-0.1	0.3
4.7	19403.5	19403.4	+0.1	0.4
5.7	21042.9	21042.7	+0.2	0.6
6.7	21997.2	21999.8	-2.6	1.0
7.7	22605.5	22607.0	-1.5	?
8.7	23021.8	23020.3	+1.5	?

3. Potassium.

PRINCIPAL SERIES (1st Component).

$$\log a_1 = 4.94821 - 10 \quad \nu_\infty = 35030.0$$

$$\log b_1 = 4.75966_n - 10$$

$(m + \mu)$	ν obs.	ν comp.	Obs. - Comp.	Limits of Error of Obs.
2.4	12988.2	12991.0	-2.8	8.5
3.4	24707.5	24705.2	+2.3	0.2
4.4	29006.6	29009.2	-2.6	0.3
5.4	31077.5	31078.6	-1.1	0.3
6.4	32233.4	32235.2	-1.8	1.0
7.4	32949.6	32947.9	+1.7	1.1
8.4	33418.8	33418.5	+0.3	1.6
9.4	33746.2	33745.4	+0.8	2.4
10.4	33981.2	33982.1	-0.9	11.6

1. SUBSIDIARY SERIES (2nd Component).

$$\log a_1 = 4.93963 - 10 \quad \nu_\infty = 22049.8$$

$$\log b_1 = 4.86438_n - 10$$

$(m + \mu)$	ν obs.	ν comp.	Obs. - Comp.	Limits of Error of Obs.
4.0	14469.3	14469.3	0.0	1.0
5.0	17293.0	17293.0	0.0	0.2
6.0	18784.5	18781.5	+3.0	0.5
7.0	19667.7	19663.7	+4.0	0.8
8.0	20230.2	20230.4	-0.2	4.2
9.0	20616.9	20616.3	+0.6	?
10.0	20883.8	20890.9	-7.1	?

2. SUBSIDIARY SERIES (1st Component).

$$\log a_1 = 4.92834 - 10 \quad \nu_\infty = 21996.9$$

$$\log b_1 = 4.76493_n - 10$$

$(m + \mu)$	ν obs.	ν comp.	Obs. - Comp.	Limits of Error of Obs.
5.0	17146.1	17146.2	-0.1	0.2
6.0	18657.1	18657.1	0.0	0.5
7.0	19559.2	19555.8	+3.4	0.8
8.0	20139.0	20134.1	+4.9	4.1
9.0	20532.2	20528.4	+3.8	?
10.0	20796.9	20809.3	-12.4	?
11.0	21011.1	21016.6	-5.5	?

4. Rubidium.

PRINCIPAL SERIES (1st } Component).

$$\log a_1 = \begin{cases} 4.92680 - 10 \\ 4.92935 - 10 \end{cases} \quad \nu_\infty = \begin{cases} 33762.6 \\ 33754.7 \end{cases}$$

$$\log b_1 = \begin{cases} 4.99618_n - 10 \\ 4.98695_n - 10 \end{cases}$$

$(m + \mu)$	ν obs.	ν comp.	Obs. - Comp.	Limits of Error of Obs.
2.6	$\begin{cases} 12577.9 \\ 12810.7 \end{cases}$	$\begin{cases} 12578.1 \\ 12810.7 \end{cases}$	$\begin{cases} -0.2 \\ 0.0 \end{cases}$	$\begin{cases} 0.5 \\ 0.8 \end{cases}$
3.6	$\begin{cases} 23720.7 \\ 23798.3 \end{cases}$	$\begin{cases} 23720.9 \\ 23798.2 \end{cases}$	$\begin{cases} -0.2 \\ +0.1 \end{cases}$	$\begin{cases} 0.2 \\ 0.2 \end{cases}$
4.6	$\begin{cases} 27841.7 \\ 27876.7 \end{cases}$	$\begin{cases} 27840.9 \\ 27876.8 \end{cases}$	$\begin{cases} +0.8 \\ -0.1 \end{cases}$	$\begin{cases} 0.4 \\ 0.4 \end{cases}$
5.6	$\begin{cases} 29841.6 \\ 29860.9 \end{cases}$	$\begin{cases} 29841.8 \\ 29860.9 \end{cases}$	$\begin{cases} -0.2 \\ 0.0 \end{cases}$	$\begin{cases} 0.5 \\ 0.5 \end{cases}$

SUBSIDIARY SERIES (2nd Component).

$$\log a_1 = 4.90803 - 10 \quad \nu_\infty = 21203.3$$

$$\log b_1 = 4.76895_n - 10$$

$(m + \mu)$	ν obs.	ν comp.	Obs. - Comp.	Limits of Error of Obs.
4.0	13111.9	13111.9	0.0	0.9
5.0	16111.6	16111.9	-0.3	0.5
6.0	17704.8	17699.6	+5.2	0.5
7.0	18646.5	18643.2	+3.3	0.7
8.0	19250.0	19250.0	0.0	?
9.0	19662.6	19663.6	-1.0	?

5. Cæsium.

PRINCIPAL SERIES (1st } Component).

$$\log a_1 = \begin{cases} 4.90783 - 10 \\ 4.91436 - 10 \end{cases} \quad \nu_\infty = \begin{cases} 31525.6 \\ 31496.5 \end{cases}$$

$$\log b_1 = \begin{cases} 5.15453_n - 10 \\ 5.13949_n - 10 \end{cases}$$

$(m + \mu)$	ν obs.	ν comp.	Obs. - Comp.	Limits of Error of Obs.
2.8	$\begin{cases} 11173.3 \\ 11726.5 \end{cases}$	$\begin{cases} 11173.3 \\ 11726.5 \end{cases}$	$\begin{cases} 0.0 \\ 0.0 \end{cases}$	$\begin{cases} 1.0 \\ 0.5 \end{cases}$
3.8	$\begin{cases} 21770.7 \\ 21951.8 \end{cases}$	$\begin{cases} 21770.9 \\ 21951.7 \end{cases}$	$\begin{cases} -0.2 \\ +0.1 \end{cases}$	$\begin{cases} 0.2 \\ 0.2 \end{cases}$
4.8	$\begin{cases} 25714.7 \\ 25794.9 \end{cases}$	$\begin{cases} 25714.0 \\ 25794.5 \end{cases}$	$\begin{cases} +0.7 \\ +0.4 \end{cases}$	$\begin{cases} 0.6 \\ 0.6 \end{cases}$
5.8	$\begin{cases} 27646.6 \\ 27686.7 \end{cases}$	$\begin{cases} 27646.7 \\ 27685.7 \end{cases}$	$\begin{cases} -0.1 \\ +1.0 \end{cases}$	$\begin{cases} 2.3 \\ 1.6 \end{cases}$

5. Cæsium—*continued*.

SUBSIDIARY SERIES (1st Component).

$$\begin{aligned}\log a_1 &= 4.90651 - 10 & \nu_\infty &= 19747.6 \\ \log b_1 &= 5.21884_n - 10\end{aligned}$$

$(m + \mu)$	ν obs.	ν comp.	Obs. - Comp.	Limits of Error of Obs.
4.0	10855.6	10855.6	0.0	0.8
5.0	14339.2	14343.1	- 3.9	10.0
6.0	16094.2	16094.3	- 0.1	1.3
7.0	17108.4	17106.0	+ 2.4	1.5
8.0	17745.9	17745.6	+ 0.3	1.6
9.0	18175.5	18176.7	- 1.2	?
10.0	18481.2	18481.4	- 0.2	?
11.0	18705.9	18705.0	+ 0.9	?

I have omitted the second subsidiary series of Rubidium, of which only three lines are known, the series being thus insufficient for determining all the constants. It is, I think, obvious, and scarcely requires to be mentioned, that the principal series of Rubidium and Cæsium, in which the four unknowns of our equation had to be computed from the only four lines available, can tell us nothing of the accuracy of the formula employed. But for obvious reasons I have made it a rule to compute every series from which all the four constants may be obtained.

Let us now, before we proceed to other groups of elements, investigate the residuals given in the columns [Obs. - Comp.], by comparing them with those of the hitherto best empirical formula, that proposed by KAYSER and RUNGE :

$$10^8\lambda^{-1} = a + bm^{-2} + cm^{-4}.$$

This equation apparently contains three unknown constants, a , b , and c , and seems therefore to possess in this respect an advantage over ours, which has four unknown quantities. But it is well to consider that a fourth unknown is implicitly involved in KAYSER's formula, viz. the value of m for the first line of the series, which we may call m_1 . Strictly speaking, the difference between KAYSER's formula and the one here proposed is therefore this, that the fourth unknown m_1 in the former is an integer, while in the latter it is a compound fraction. But let us grant to Professor KAYSER's equation the full advantage of having one unknown less than ours. If it would represent the observations equally well, it would doubtless be the superior formula. This condition, however, is far from being fulfilled. Let us, for instance, consider the principal series of Potassium. Professor KAYSER has computed the three unknowns of his equation by the method of least squares, and has found the residuals, expressed in units of wave-lengths, which are given in the first column of the following table,

while the second column contains, in the same units, the residuals computed from the RYDBERG-THIELE formula :

+ 2.7	+ 1.6	+ 161.3	+ 172
- 3.6	- 0.4	0.0	0.0
+ 1.6	+ 0.3	0.0	0.0
+ 1.3	+ 0.1	0.0	- 0.1
+ 0.8	+ 0.2	+ 0.3	+ 0.1
- 0.3	- 0.1	+ 0.2	0.0
- 0.4	0.0	+ 0.7	+ 0.4
- 0.5	- 0.1	+ 1.0	+ 0.8
- 0.5	+ 0.1	+ 1.4	+ 1.1

A comparison of the two columns shows the considerable superiority of the RYDBERG-THIELE formula. Indeed, the representation of the observed wave-lengths by KAYSER's formula appeared to Professor KAYSER himself so little satisfactory that he abandoned this method of computing the constants. In order to obtain more reliable values of these, he disregarded the first line and computed his equation from the second, third and fourth lines only. The residuals in this case are given in the third column. In another calculation, the result of which is represented in the residuals of the fourth column, he computed the constants from all the lines except the first. We observe that in both cases his endeavour to improve the shorter wave-lengths was defeated, notwithstanding the sacrifice of the first line, which shows an enormous discordance. The computations demonstrate clearly that KAYSER's formula cannot be made to represent the observed wave-lengths nearly so well as the RYDBERG-THIELE equation, although the discrepancies of this latter, in the special case considered, are much greater than usual.

But it may be urged that the introduction of another unknown in KAYSER's formula might improve matters. To decide this point, let us consider the more general equation

$$10^8\lambda^{-1} = a + bm^{-2} + cm^{-4} + dm^{-6}.$$

I have computed the numerical forms of this equation for the principal series of Li, Na and K, by using first the 1., 3., 5. and 7. lines of the series, and obtained the following equations :

$$\text{Li : } 10^8\lambda^{-1} = 43552.5 - 130802 m^{-2} - 1156838 m^{-4} + 124237 m^{-6}$$

$$\text{Na : } 10^8\lambda^{-1} = 41516.7 - 128378 m^{-2} - 829617 m^{-4} - 36437 m^{-6}$$

$$\text{K : } 10^8\lambda^{-1} = 35075.6 - 126522 m^{-2} - 618583 m^{-4} - 287275 m^{-6}$$

The residuals, expressed in units of wave-frequency, are shown in the subjoined table under the heading K-R, while those of the RYDBERG-THIELE formula are repeated from the preceding tables and given under Ry-Th.

Li.		Na.		K.	
K-R.	Ry-Th.	K-R.	Ry-Th.	K-R.	Ry-Th.
0.0	+0.1	0.0	0.0	0.0	-2.8
+44.4	+0.4	+31.5	0.0	+26.0	+2.3
0.0	+2.1	0.0	+0.2	0.0	-2.6
-6.3	+0.4	-2.7	-0.2	-0.1	-1.1
0.0	+2.8	0.0	-0.1	0.0	-1.8
+0.8	+1.8	+2.4	+1.3	+3.0	+1.7
0.0	+0.2	0.0	+0.5	0.0	+0.3
-4.1	-2.9			-2.0	+0.8
-8.8	-5.5			-6.3	-0.9

The enormous discrepancies in the second lines show that KAYSER's formula is still far from representing the actual phenomena, and hence, even in this extended form, is inferior to the RYDBERG-THIELE equation. To give full justice to the former I have repeated the computations by excluding the first lines, but I have come to the conclusion that while the fourth constant produces on the whole a slight improvement in the shorter wave-lengths, the discrepancies in the first lines are even increased. All these computations have convinced me that no general improvement can be expected by adding a further term to KAYSER's formula.

But besides we find other facts which speak in favour of the equation here employed. There exists a certain empirical law, first pronounced by RYDBERG and KAYSER, that if for a given element two or more subsidiary series exist, these series converge into one common tail. This law has now been confirmed approximately in so many instances, that we may accept its correctness. The presumption is warranted, therefore, that the better formula should also bear out this law more precisely. Now let us compare in this respect KAYSER's formula with the RYDBERG-THIELE equation. We find for the wave-frequencies of the tails of the 1st components :

		K-R.	Diff.	Ry-Th.	Diff.
Lithium	1. S.S.	28586.7		28594.7	
	2. S.S.	28666.7	+80.7	28583.3	-11.4
Sodium	1. S.S.	24492.3		24481.2	
	2. S.S.	24549.1	+56.8	24490.4	+9.2
Potassium	1. S.S.	21991.2		21991.8	
	2. S.S.	22021.8	+30.6	21996.9	+5.1

These figures leave no doubt that the law is represented much better by our formula than by that of KAYSER and RUNGE. We shall see later on that this applies to other spectra as well.

A scarcely less convincing test of the superiority of the RYDBERG-THIELE equation is afforded by the discussion of another empirical law which we owe to RYDBERG. This law may be expressed as follows: (see KAYSER, *H. d. S.*, p. 557). The wave-frequency of the first line of the principal series is equal to the difference of the wave-frequencies of the tails of the principal and subsidiary series. It must be remarked, however, that if we take the *first* components [*i.e.* those of greater wave-lengths] of the subsidiary series, the law refers to the *second* components [shorter wave-lengths] of the principal series. Here are the figures corresponding to the two formulæ:

	K-R.			Ry-Th.			Observed 1st Line of P.S.	Obs. - Comp.	
	P.S.	S.S.	Difference.	P.S.	S.S.	Difference.		K-R.	Ry-Th.
Li:	43584	28627	14957	43498	28589	14909	14907	- 50	- 2
Na:	41542	24521	17021	41468	24486	16982	16977	- 44	- 5
K:	35086	22006	13080	35030	21994	13036	13045	35	+ 9
Rb:	33762	20919	12843	33755	20965	12790	12811	- 32	+ 21
Cs:	31509	19743	11766	31496	19748	11748	11726	- 40	- 22

From the last two columns we see that RYDBERG's law is represented in a distinctly better manner if the RYDBERG-THIELE formula is used. More important advantages of the latter will, however, appear in a subsequent part of the investigation upon which we can enter only after having examined the line-series of the other elements.

Of the remaining elements of the first vertical column in MENDELEJEFF's series we can investigate here only Silver, of which four lines of the 1st subsidiary series are known. This being the minimum number of lines necessary for computing the constants of our equation, we must omit those series in which less than four lines have been observed. Doubtless in some of these cases three lines would be sufficient, because we have seen already that in a considerable number of series $\mu = 0$ or $(m + \mu)$ an integer, so that our equation contains only three unknowns. But to decide whether the series belongs to this special group we still require at least four data.

6. Silver.

1st SUBSIDIARY SERIES (1st Component).

$$\log a_1 = 4.96094 - 10$$

$$\nu_\infty = 30646.4$$

$$\log b_1 = 4.15268_n - 10$$

$(m + \mu)$	ν obs.	ν comp.	Obs. - Comp.
3.0	18275.8	18275.8	0.0
4.0	23741.1	23741.1	0.0
5.0	26242.6	26242.6	0.0
6.0	27593.7	27594.0	- 0.3

It is of course quite unnecessary to compute the equation for more than one component in those cases where the subsidiary series consists of double or triple lines, because it is well known that the difference between the wave-frequencies of corresponding components is constant throughout the series. We therefore obtain the equation of the second or third component from that of the first by simply adding a constant to ν_∞ .

We now turn to the elements of the second vertical column of MENDELEJEV'S series. The tables are computed in the same manner as before, but I have added a column showing the residuals of KAYSER'S formula which have been taken from the data in his *Handbuch*, but have been converted into wave-frequencies. The structure of the triplets in the 1st subsidiary series is in many cases complicated, especially that of the first two components. In such instances my computations refer to the simpler third components:

7. Magnesium.

1. SUBSIDIARY SERIES (1st Component).

$$\begin{aligned}\log a_1 &= 4.95065 - 10 & \nu_\infty &= 39779.3 \\ \log b_1 &= 4.34688_n - 10\end{aligned}$$

$(m + \mu)$	ν obs.	ν comp.	Obs. - Comp.	K-R.
2.9	26052.2	26051.3	+0.9	+0.1
3.9	32288.7	32290.9	-2.2	-0.1
4.9	35065.1	35064.2	+0.9	-3.9
5.9	36538.5	36537.6	+0.9	0.0
6.9	37412.6	37413.7	-1.1	+3.5
7.9	37977.6	37976.9	+0.7	+9.7

2. SUBSIDIARY SERIES (1st Component).

$$\begin{aligned}\log a_1 &= 4.94696 - 10 & \nu_\infty &= 39780.2 \\ \log b_1 &= 4.81358_n - 10\end{aligned}$$

$(m + \mu)$	ν obs.	ν comp.	Obs. - Comp.	K-R.
2.5	19290.7	19290.2	+0.5	-198.0
3.5	29968.6	29967.5	+1.1	+ 0.3
4.5	33988.1	33990.2	-2.1	- 0.5
5.5	35951.4	35951.9	-0.5	+ 0.2
6.5	37058.5	37058.6	-0.1	- 1.5
7.5	37745.8	37744.9	+0.9	- 3.8

8. Calcium.

1. SUBSIDIARY SERIES (3rd Component).

$$\begin{aligned}\log a_1 &= 4.95797 - 10 & \nu_\infty &= 34073.0 \\ \log b_1 &= 4.76493_n - 10\end{aligned}$$

$(m + \mu)$	ν obs.	ν comp.	Obs. - Comp.	K-R.
3.2	22595.9	22596.4	- 0.5	- 0.3
4.2	27592.5	27592.5	0.0	- 0.5
5.2	29900.0	29900.0	0.0	0.0
6.2	31155.0	31158.6	- 3.6	+ 3.8
7.2	31886.4	31921.4	- 35.0	- 21.8

2. SUBSIDIARY SERIES (1st Component).

$$\begin{aligned}\log a_1 &= 4.94860 - 10 & \nu_\infty &= 34001.7 \\ \log b_1 &= 4.92942_n - 10\end{aligned}$$

$(m + \mu)$	ν obs.	ν comp.	Obs. - Comp.	K-R.
2.7	16227.4	16227.6	-0.2	-158.
3.7	25164.1	25161.3	+2.8	0.0
4.7	28671.3	28675.0	-3.7	0.0
5.7	30430.0	30431.9	-1.9	- 0.2
6.7	31432.9	31440.3	-7.4	- 21.6
7.7	32073.9	32072.0	+1.9	+ 5.1

9. Strontium.

1. SUBSIDIARY SERIES (3rd Component).

$$\log a_1 = 4.93097 - 10 \quad \nu_\infty = 31640.3$$

$$\log b_1 = 5.11861_n - 10$$

$(m + \mu)$	ν obs.	ν comp.	Obs. - Comp.	K-R.
3.5	20694.3	20694.3	0.0	+ 0.7
4.5	25374.7	25374.8	- 0.1	- 2.6
5.5	27554.4	27557.1	- 2.7	- 11.7
6.5	28758.0	28760.6	- 2.6	- 9.5
7.5	29498.0	29497.5	+ 0.5	+ 3.1
8.5	29987.9*	29982.4	+ 5.5	+ 16.3

2. SUBSIDIARY SERIES (1st Component).

$$\log a_1 = 4.93049 - 10 \quad \nu_\infty = 31077.7$$

$$\log b_1 = 5.10018_n - 10$$

$(m + \mu)$	ν obs.	ν comp.	Obs. - Comp.	K-R.
2.9	14142.9	14142.9	0.0	- 96.
3.9	22531.5	22530.1	+ 1.4	+ 0.1
4.9	25868.7	25868.7	0.0	- 2.2
5.9	27559.0	27556.5	+ 2.5	- 0.1
6.9	28533.3	28533.3	0.0	- 2.2

The enormous discrepancies in the first lines of the 2nd subsidiary series shown by Professor KAYSER's formula might, as in similar cases before, be considerably reduced by employing these lines in the computation of the constants. But this would involve inadmissible residuals in the shorter wave-lengths. It may be shown by easy calculations that no numerical form of KAYSER's equation can represent the observed wave-frequencies with the same accuracy as the RYDBERG-THIELE formula. After the foregoing discussion of the relative merits of the two formulæ I need not dwell upon this point any longer. The shortest wave-length of the 1st series of calcium is badly represented by both equations; and although KAYSER's formula is distinctly better than ours, neither formula is satisfactory. It is worthy of note that there are two other instances, viz. the first series of Aluminium and the second series of Thallium, where both equations distinctly fail.

10. Zinc.

1. SUBSIDIARY SERIES (1st Component).

$$\log a_1 = 4.94561 - 10 \quad \nu_\infty = 42918.6$$

$$\log b_1 = 4.43373_n - 10$$

$(m + \mu)$	ν obs.	ν comp.	Obs. - Comp.	K-R.
3.0	29889.3	29889.2	+ 0.1	+ 0.7
4.0	35701.7	35701.6	+ 0.1	- 0.3
5.0	38333.3	38332.0	+ 1.3	- 0.9
6.0	39745.5	39745.5	0.0	+ 1.8
7.0	40592.7	40592.7	0.0	+ 6.5
8.0	41140.0	41140.6	- 0.6	...

2. SUBSIDIARY SERIES.

$$\log a_1 = 4.93860 - 10 \quad \nu_\infty = 42924.5$$

$$\log b_1 = 4.84137_n - 10$$

$(m + \mu)$	ν obs.	ν comp.	Obs. - Comp.	K-R.
2.45	20787.0	20787.0	0.0	- 251.
3.45	32550.0	32550.5	- 0.5	0.0
4.45	36864.0	36863.1	+ 0.9	- 0.2
5.45	38940.0	38939.2	+ 0.8	+ 0.2
6.45	40101.0	40101.5	- 0.5	+ 0.6
7.45	40820.0	40818.4	+ 1.6	+ 3.3

* The line observed is the first component: $\nu = 29408.0$.

11. Cadmium.

1. SUBSIDIARY SERIES (3rd Component).

$$\log a_1 = 4.95027 - 10 \quad \nu_\infty = 42450.4$$

$$\log b_1 = 4.56211_n - 10$$

$(m + \mu)$	ν obs.	ν comp.	Obs. - Comp.	K-R.
3.0	29379.3	29379.3	0.0	+ 0.1
4.0	35248.3	35248.3	0.0	+ 0.5
5.0	37884.5	37884.5	0.0	- 4.1
6.0	39294.5	39299.8	- 5.3	+ 1.0
7.0	40137*	40142.8	- 5.8	+ 5.3

2. SUBSIDIARY SERIES (1st Component).

$$\log a_1 = 4.93417 - 10 \quad \nu_\infty = 40765.7$$

$$\log b_1 = 4.92926_n - 10$$

$(m + \mu)$	ν obs.	ν comp.	Obs. - Comp.	K-R.
2.55	19661.9	19661.0	+ 0.9	- 263.
3.55	30744.8	30746.5	- 1.7	- 0.1
4.55	34863.3	34862.9	+ 0.4	+ 0.2
5.55	36864.0	36862.7	+ 1.3	- 0.3
6.55	37989.0	37989.3	- 0.3	1.7
7.55	38716.7	38688.3	+ 28.4	+ 26.3
8.55	39141.0	39152.1	- 11.1	...

12. Mercury.

1. SUBSIDIARY SERIES (3rd Component).

$$\log a_1 = 4.95111 - 10 \quad \nu_\infty = 46582.5$$

$$\log b_1 = 4.44885_n - 10$$

$(m + \mu)$	ν obs.	ν comp.	Obs. - Comp.	K-R.
3.0	33698.5	33696.8	+ 1.7	...
4.0	39449.0	39447.5	+ 1.5	...
5.0	42045.0	42048.9	- 3.9	...
6.0	43448.0	43446.4	+ 1.6	...

2. SUBSIDIARY SERIES (1st Component).

$$\log a_1 = 4.94401 - 10 \quad \nu_\infty = 40168.2$$

$$\log b_1 = 4.84592_n - 10$$

$(m + \mu)$	ν obs.	ν comp.	Obs. - Comp.	K-R.
2.45	18311.7	18311.7	0.0	- 191.
3.45	29924.7	29923.9	+ 0.8	+ 0.1
4.45	34182.3	34182.5	- 0.2	- 0.2
5.45	36234.2	36232.6	+ 1.6	- 0.6
6.45	37380.3	37380.3	0.0	- 3.4

Turning to the elements of the 3rd column of MENDELEJEV'S series, we find Al, In and Tl each with two subsidiary series. I have mentioned already that unexplained anomalies exist in the first series of Al and the second series of Tl, and that neither KAYSER'S formula nor the present one represents the observed lines in a satisfactory manner. Professor KAYSER has nevertheless partly reconciled his formula with the observations by neglecting in each case the first three lines, and by demonstrating that the remainder could thereby be brought into fairly satisfactory agreement. It might be easily shown that under these circumstances our formula would render equally good service. But as long as the nature of these quite exceptional discrepancies is unknown, I consider such computations as being of little value. I am inclined to think that the series referred to are not homogeneous, but are in fact the result of a superposition of several branches, perhaps two in each case, which coalesce in such a manner as to give the impression of one single series. We shall come upon such anomalous cases later on when treating of the band-series, where in at least one instance, viz. the cyanogen-band, the hetero-

* Computed from the 2nd component : $\nu = 39594.5$.

geneous character of what to all appearance seems a single series can be proved. Leaving this point in abeyance for the present, we shall disregard the two discrepant series.

13. Aluminium.

2. SUBSIDIARY SERIES (1st Component).

$$\log a_1 = 4.94086 - 10 \quad \nu_\infty = 48208.0$$

$$\log b_1 = 4.82757_n - 10$$

$(m + \mu)$	ν obs.	ν comp.	Obs. - Comp.	K-R.
2.4	25242.2	25242.2	0.0	-338
3.4	37587.3	37587.8	-0.5	0.0
4.4	42043.6	42043.9	-0.3	0.0
5.4	44172.0	44171.4	+0.6	0.0
6.4	45356.7	45356.8	-1.0	+1.7

14. Indium.

1. SUBSIDIARY SERIES (2nd Component).

$$\log a_1 = 4.92091 - 10 \quad \nu_\infty = 46706.8$$

$$\log b_1 = 4.41282_n - 10$$

$(m + \mu)$	ν obs.	ν comp.	Obs. - Comp.	K-R.
3.0	32900	32900	0	0
4.0	39060	39060	0	0
5.0	41847	41847	0	0
6.0	43350	43345	+5	+11
7.0	44236	44243	-7	+2
8.0	44825	44823	+2	+16
9.0	45224	45220	+4	+20
10.0	45506	45502	+4	+19
11.0	45714	45713	+1	+17
12.0	45871	45872	-1	+13

Indium—continued.

2. SUBSIDIARY SERIES (2nd Component).

$$\log a_1 = 4.93998 - 10 \quad \nu_\infty = 46709.8$$

$$\log b_1 = 4.87482_n - 10$$

$(m + \mu)$	ν obs.	ν comp.	Obs. - Comp.	K-R.
2.45	24379	24379	0	-333
3.45	36311	36311	0	0
4.45	40648	40648	0	0
5.45	42730	42729	+1	0
6.45	43891	43891	0	-2
7.45	44611	44609	+2	+2
8.45	45080	45082	-2	-6
9.45	45455	45412	+43	+39

15. Thallium.

1. SUBSIDIARY SERIES (1st Component).

$$\log a_1 = 4.94304 - 10 \quad \nu_\infty = 41511.7$$

$$\log b_1 = 4.48629_n - 10$$

$(m + \mu)$	ν obs.	ν comp.	Obs. - Comp.	K-R.
3.0	28332	28332	0	0
4.0	34228	34227	+1	+1
5.0	36887	36887	0	-2
6.0	38316	38314	+2	0
7.0	39168	39168	0	+2
8.0	39722	39721	+1	+5
9.0	40096	40098	-2	+3
10.0	40362	40363	-1	-1
11.0	40559	40567	-8	-4
12.0	40708	40718	-10	-7
13.0	40824	40836	-12	-11
14.0	40916	40929	-13	-13
15.0	40991	41005	-14	-16

To complete our investigation of the line-spectra we will now discuss the line-series observed by RUNGE and PASCHEN in the spectra of Oxygen, Sulphur and Selenium (*Astrophysical Journal*, vol. viii.), and in the spectrum of Helium (KAYSER, *Handbuch*, pp. 560-1). The comparison of these series with the RYDBERG-THIELE formula is specially interesting, not only on account of the extreme accuracy of the observations which thereby afford a valuable test of this formula, but still more because it had been

found that KAYSER's formula, in its original form, did not sufficiently satisfy the measurements, which had to be represented by an equation of the form

$$10^3\lambda^{-1} = a + bm^{-2} + cm^{-3}.$$

This modification must of necessity complicate the theoretical aspect of the problem, inasmuch as the line-series would appear to be of two different types, in which the structure of the series is seemingly determined by different conditions. But we shall see now that the series of all these elements are represented by the same type of the RYDBERG-THIELE equation which we had employed in the foregoing discussion, and hence that a separation in two different types, such as is demanded by KAYSER's formula, is not required. This must be considered as an important advantage in our equation, which will become more apparent in the later discussion of the results.

16. Oxygen.

1st TRIPLET SERIES (1st Component).

$$\begin{aligned} \log a_1 &= 4.95404 - 10 & \nu_\infty &= 23212.5 \\ \log b_1 &= 3.80598_n - 10 \end{aligned}$$

$(m + \mu)$	ν obs. (reduced to vacuum).	ν comp.	Obs. - Comp.	R-P. (l.c. p. 76).
4.0	16233.5	16233.9	-0.4	0.0
5.0	18753.6	18753.4	+0.2	-0.3
6.0	20119.5	20118.6	+0.9	+0.2
7.0	20941.3	20940.6	+0.7	+0.2
8.0	21473.9	21473.6	+0.3	+0.2
9.0	21838.4	21838.9	-0.5	-0.2
10.0	22099.7	22100.1	-0.4	+0.5

2nd TRIPLET SERIES (1st Component).

$$\begin{aligned} \log a_1 &= 4.95750 - 10 & \nu_\infty &= 23207.3 \\ \log b_1 &= 4.16157_n - 10 \end{aligned}$$

$(m + \mu)$	ν obs. (reduced to vacuum).	ν comp.	Obs. - Comp.	R-P. (l.c. p. 77).
3.8	15484.6	15484.6	0.0	-0.3
4.8	18387.3	18387.3	0.0	+1.0
5.8	19913.6	19913.4	+0.2	-0.1
6.8	20813.8	20814.0	-0.2	-0.8
7.8	21389.6	21389.9	-0.3	-0.2
8.8	21780.2	21780.3	-0.1	+0.9

Oxygen—continued.

1st PAIR SERIES (1st Component).

$$\begin{aligned} \log a_1 &= 4.96523 - 10 & \nu_\infty &= 21201.7 \\ \log b_1 &= 4.16168 - 10 \end{aligned}$$

$(m + \mu)$	ν obs. (red. to vac.)	ν comp.	Obs. - Comp.	R-P. (l.c. p. 81).
3.8	13781.2	13781.5	-0.3	-0.2
4.8	16533.8	16532.4	+1.4	+0.9
5.8	17996.4	17996.5	-0.1	-0.4
6.8	18865.7	18867.0	-1.3	-1.1
7.8	19426.4	19425.5	+0.9	+0.9
8.8	19804.9	19805.6	-0.7	-0.6
9.8	20075.9	20075.6	+0.3	+0.5

2nd PAIR SERIES (1st Component).

$$\begin{aligned} \log a_1 &= 4.95587 - 10 & \nu_\infty &= 21212.7 \\ \log b_1 &= 3.55793_n - 10 \end{aligned}$$

$(m + \mu)$	ν obs. (red. to vac.)	ν comp.	Obs. - Comp.	R-P. (l.c. p. 81).
4.0	14276.8	14276.7	+0.1	+0.2
5.0	16777.5	16777.7	-0.2	-0.4
6.0	18134.3	18134.3	0.0	-0.5
7.0	18951.3	18951.8	-0.5	-0.8
8.0	19485.2	19482.0	+3.2	+3.0
9.0	19846.3	19845.4	+0.9	+0.8
10.0	20102.9	20105.4	-2.5	-2.3

17. Sulphur.

1st TRIPLET SERIES (1st Component).

$\log a_1 = 4.96004 - 10$

$\nu_\infty = 20085.9$

$\log b_1 = 4.63201 - 10$

$(m + \mu)$	ν obs. (red. to vac.)	ν comp.	Obs. - Comp.	R-P. (l.c. p. 87).
4.5	14794.6	14794.5	+0.1	+0.1
5.5	16516.3	16517.0	-0.7	-0.5
6.5	17519.3	17519.5	-0.2	+0.1
7.5	18153.1	18152.9	+0.2	+0.5
8.5	18578.2	18578.2	0.0	+0.1
9.5	18877.4	18877.4	0.0	+0.2

2nd TRIPLET SERIES (1st Component).

$\log a_1 = 4.95431 - 10$

$\nu_\infty = 20089.4$

$\log b_1 = 4.49826_n - 10$

$(m + \mu)$	ν obs. (red. to vac.)	ν comp.	Obs. - Comp.	R-P. (l.c. p. 88).
5.0	15582.6	15582.7	-0.1	+0.1
6.0	16973.1	16973.2	-0.1	-0.1
7.0	17806.2	17805.9	+0.3	+0.4
8.0	18343.6	18344.0	-0.4	+0.1

18. Selenium.

1st TRIPLET SERIES (1st Component).

$\log a_1 = 4.97128 - 10$

$\nu_\infty = 19257.8$

$\log b_1 = 4.81092 - 10$

$(m + \mu)$	ν obs. (red. to vac.)	ν comp.	Obs. - Comp.	R-P. (l.c. p. 94).
4.5	14156.2	14156.4	-0.2	0.0
5.5	15805.0	15804.8	+0.2	0.0
6.5	16769.2	16769.8	-0.6	0.0
7.5	17379.6	17381.6	-2.0	-1.2
8.5	17794.9	17793.3	+1.6	+2.2
9.5	18083.2	18083.0	+0.2	-0.6
10.5	18293.9	18294.7	-0.8	-1.8

Selenium—continued.

2nd TRIPLET SERIES (1st Component).

$\log a_1 = 4.95145 - 10$

$\nu_\infty = 19286.2$

$\log b_1 = 3.40040 - 10$

$(m + \mu)$	ν obs. (red. to vac.)	ν comp.	Obs. - Comp.	R-P. (l.c. p. 95).
5.0	14818.2	14818.2	0.0	0.0
6.0	16182.4	16182.3	+0.1	0.0
7.0	17005.4	17005.3	+0.1	0.0
8.0	17538.1	17539.5	-1.4	-1.7

19. Helium.

1st PRINCIPAL SERIES.

$\log a_1 = 4.95902 - 10$

$\nu_\infty = 38465.9$

$\log b_1 = 3.11561 - 10$

$(m + \mu)$	ν obs.	ν comp.	Obs. - Comp.	K-R.
$2\frac{1}{2}$	25715.3	25715.3	0.0	0.0
$3\frac{1}{2}$	31369.2	31369.2	0.0	0.0
$4\frac{1}{2}$	33953.1	33953.2	-0.1	0.0
$5\frac{1}{2}$	35345.8	35345.6	+0.2	+0.2
$6\frac{1}{2}$	36180.7	36180.5	+0.2	-0.1
$7\frac{1}{2}$	36720.8	36720.2	+0.6	-0.1
$8\frac{1}{2}$	37088.3	37089.1	-0.8	-0.7
$9\frac{1}{2}$	37352.5	37353.2	-0.7	-0.3
$10\frac{1}{2}$	37547.5	37546.7	-0.8	+0.3

1st SUBSIDIARY SERIES (2nd Component).

$\log a_1 = 4.95913 - 10$

$\nu_\infty = 29231.6$

$\log b_1 = 2.60695_n - 10$

$(m + \mu)$	ν obs.	ν comp.	Obs. - Comp.	K-R.
3.0	17018.8	17018.8	0.0	0.0
4.0	22363.5	22363.3	+0.2	0.0
5.0	24836.5	24836.3	+0.2	0.0
6.0	26180.0	26179.5	+0.5	-0.1
7.0	26989.4	26989.4	0.0	-0.3
8.0	27515.0	27514.9	+0.1	-0.5
9.0	27875.3	27875.2	+0.1	-0.7
10.0	28133.3	28133.0	+0.3	-1.1
11.0	28323.8	28323.6	+0.2	-1.0
12.0	28468.7	28468.6	+0.1	-1.0
13.0	28581.3	28581.5	-0.2	-1.0
14.0	28670.7	28670.9	-0.2	-1.2
15.0	28743.3	28743.3	0.0	-1.2
16.0	28802.7	28802.5	+0.2	-1.0
17.0	28851.3	28851.5	-0.2	-1.1
18.0	28890.0	28892.5	-2.5	-3.4
19.0	28927.3	28927.3	0.0	-0.7

Helium—continued.

2nd SUBSIDIARY SERIES (2nd Component).

$$\log a_1 = 4.96066 - 10 \quad \nu_\infty = 29229.2$$

$$\log b_1 = 3.40436 - 10$$

$(m + \mu)$	ν obs.	ν comp.	Obs. - Comp.	K-R.
2.7	14153.3	14153.7	-0.4	-48.
3.7	21216.7	21216.0	+0.7	0.0
4.7	24266.1	24267.0	-0.9	0.0
5.7	25855.9	25856.6	-0.7	0.0
6.7	26788.1	26788.9	-0.8	+1.4
7.7	27381.2	27381.8	-0.6	+3.5
8.7	27781.9	27782.2	-0.3	+5.5
9.7	28065.3	28065.3	0.0	+7.6
10.7	28272.7	28272.7	0.0	+9.3
11.7	28429.4	28429.3	+0.1	+10.7
12.7	28550.7	28550.3	+0.4	+12.7
13.7	28647.3	28645.8	+1.5	+14.1
14.7	28722.5	28722.5	0.0	+14.0

2nd PRINCIPAL SERIES.

$$\log a_1 = 4.96161 - 10 \quad \nu_\infty = 32036.9$$

$$\log b_1 = 3.40531 - 10$$

$(m + \mu)$	ν obs.	ν comp.	Obs. - Comp.	K-R.
3.0	19936.8	19936.4	+0.4	0.0
4.0	25221.1	25221.1	0.0	0.0
5.0	27671.3	27672.1	-0.8	0.0
6.0	29004.5	29004.9	-0.4	+0.2
7.0	29809.3	29808.8	+0.5	+0.7
8.0	30331.3	30330.8	+0.5	+0.7
9.0	30690.7	30688.7	+2.0	+1.5
10.0	30947.1	30944.8	+2.3	+1.8
11.0	31136.4	31134.3	+2.1	+2.1
12.0	31280.7	31278.4	+2.3	+2.0
13.0	...	...	...	...
14.0	31480.7	31479.6	+1.1	-0.4

Helium—continued.

3rd SUBSIDIARY SERIES.

$$\log a_1 = 4.95930 - 10 \quad \nu_\infty = 27182.4$$

$$\log b_1 = 2.60712 - 10$$

$(m + \mu)$	ν obs.	ν comp.	Obs. - Comp.	K-R.
3.0	14973.4	14973.6	-0.2	0.0
4.0	20316.7	20316.5	+0.2	0.0
5.0	22789.0	22788.6	+0.4	0.0
6.0	24131.7	24131.4	+0.3	0.0
7.0	24941.2	24940.9	+0.3	0.0
8.0	25466.5	25466.3	+0.2	+0.1
9.0	25826.3	25826.5	-0.2	-0.2
10.0	26084.4	26084.2	+0.2	-0.2
11.0	26274.7	26274.7	0.0	-0.2
12.0	26420.0	26419.7	+0.3	-0.3
13.0	26531.9	26532.5	-0.6	-0.4
14.0	26621.9	26622.0	-0.1	-0.1

4th SUBSIDIARY SERIES.

$$\log a_1 = 4.95932 - 10 \quad \nu_\infty = 27181.7$$

$$\log b_1 = 3.67610 - 10$$

$(m + \mu)$	ν obs.	ν comp.	Obs. - Comp.	K-R.
$\frac{21}{1} \frac{3}{3}$	13732.8	13732.8	0.0	-15.8
$\frac{31}{1} \frac{3}{3}$	19810.9	19810.7	+0.2	0.0
$\frac{41}{1} \frac{3}{3}$	22534.2	22534.6	-0.4	0.0
$\frac{51}{1} \frac{3}{3}$	23986.1	23986.1	0.0	0.0
$\frac{61}{1} \frac{3}{3}$	24849.4	24850.1	-0.7	+0.4
$\frac{71}{1} \frac{3}{3}$	25405.9	25405.6	+0.3	+1.0
$\frac{81}{1} \frac{3}{3}$	25784.7	25783.9	+0.8	+1.3
$\frac{91}{1} \frac{3}{3}$	26053.7	26053.0	+0.7	+1.8
$\frac{101}{1} \frac{3}{3}$	...	...	...	...
$\frac{111}{1} \frac{3}{3}$	26401.8	26401.6	+0.2	+2.3
$\frac{121}{1} \frac{3}{3}$	26520.0	26518.1	+1.9	+4.4

Reviewing the results of the foregoing computations, which embrace now all the line-series so far as known, we must admit that the RYDBERG-THIELE formula is in many cases distinctly better than that proposed by KAYSER and RUNGE, and is never inferior to that equation. Its advantages become still more obvious if we investigate more closely the constants. Let us begin by testing the law mentioned before, according to which two subsidiary series of the same element possess common tails. In the following table we give for all cases in which two subsidiary series have been found,

the differences of the wave-frequencies of their tails, computed on the one hand by KAYSER's formula, and on the other by the RYDBERG-THIELE equation :

	K-R.	Ry-Th.		K-R.	Ry-Th.
Li :	+ 81	- 11	Hg :	+ 58	- 13
Na :	+ 57	+ 9	In :	+ 20	+ 3
K :	+ 31	+ 5	O :	- 14	- 5
Mg :	+ 41	+ 1		+ 8	+ 11
Ca :	+ 121	+ 83	S :	- 9	+ 3
Sr :	+ 35	+ 18	Se :	+ 20	+ 28
Zn :	+ 10	+ 5	He :	- 26	- 3
Cd :	+ 42	+ 17		- 7	- 1

These figures show clearly that the law in question is more closely represented by the RYDBERG-THIELE formula. Errors of 10-15 units are possibly accounted for by the uncertainty of the data from which the constants have been derived, because it can be shown that an error of only one unit in one of the observed wave-frequencies may sometimes alter the computed position of the tail by more than ten times this amount. The discrepancies in the [Ry-Th.] column, except those for Ca and Se, may therefore be considered as admissible, if the still existing uncertainties of the observed wave-lengths are taken into account.

With regard to μ , it has doubtless been noticed that in a considerable number of cases this constant is zero. Indeed, among the 44 series mentioned above we have no less than 19 instances of this kind. We find that, with the exception of Mg, Ca and Sr, all the first subsidiary series belong to this particular group, which, as has been already pointed out, includes the first Hydrogen-series. There is also evidence of the existence of smaller groups, for instance $\mu = 0.5$ [H, Mg, S, Se]. Now in any such group, if we denote by ν the wave-frequency of a line of one series and by n the wave-frequency of a line of another series, since μ is the same in both series, we have the relation

$$\frac{1}{\nu_x - \nu} = \frac{a_5}{n_x - n} + b_5 \quad (7)$$

where a_5 and b_5 are constants while ν_x and n_x are the wave-frequencies of the x th lines of the two series. This relation obviously enables us to express one series of lines by means of another belonging to the same μ -group. A similar relation obtains for the wave-lengths :

$$\frac{1}{\lambda - \lambda_x} = \frac{a_5}{l - l_x} + \beta_5 \quad (8)$$

It may be of interest to prove the existence of such a relation between the series of different spectra in some special cases. Let us take, for instance, the group $\mu = 0$, and let us assume as the series of comparison the well-known Hydrogen-series represented by BALMER's formula. In accordance with the foregoing equations, we call the wave-frequencies and wave-lengths of the hydrogen-lines n and l respectively,

those of the series to be compared ν and λ . From the considerable number of series belonging to this group we select here the following: He, 3rd S.S.; In, 1st S.S. (2nd comp.); Tl, 1st S.S. (1st comp.); Zn, 1st S.S. (2nd comp.); Li, 1st S.S. The following table contains the results of the comparison. By using equation (8) and adopting for λ_x in each case the wave-lengths which I have bracketed in the table, we find the following values of $\log \alpha_5$ and $\log \beta_5$:

	$\log \alpha_5$	$\log \beta_5$
He :	9.99165 - 10	4.50246 _n - 10
In :	0.43927	6.31899 - 10
Tl :	0.35204	6.13701 - 10
Zn :	0.39819	6.25993 - 10
Li :	0.03893	5.05185 - 10

while the computed wave-lengths as well as their discrepancies (Obs. - Comp.) are given as follows :

H.	He, 3rd S.S.	In, 1st S.S. (2nd Comp.)	Tl, 1st S.S. (1st Comp.)	Zn, 1st S.S. (2nd Comp.)	Li, 1st S.S.
6563.07	6678.37 0.00	3039.5 0.0	3529.6 0.0	3302.8 0.0	6103.8 0.0
4861.52	4922.10 0.00	2560.2 0.0	2921.6 0.0	2771.0 0.0	4602.4 0.0
4340.63	4388.07 + 0.03	2389.6 0.0	2711.1 - 0.3	2582.7 - 0.1	4132.3 + 0.1
4101.90	4143.90 + 0.02	2307.0 - 0.2	2610.2 - 0.3	2491.7 0.0	3915.1 + 0.1
3970.22	4009.41 + 0.01	2260.2 + 0.4	2553.3 - 0.2	2440.2 - 0.3	[3794.9] ...
3889.20	3926.70 - 0.02	[2230.9] ...	2517.9 - 0.4	[2408.0] ...	3720.8 - 1.9
3835.53	3871.96 - 0.01	2211.3 - 0.1	2494.2 - 0.2		3671.6 - 1.0
3798.04	3833.69 + 0.02	2197.5 0.0	[2477.6] ...		
3770.77	3805.88 + 0.02	2187.4 + 0.1	2465.4 + 0.1		
3750.30	3785.01 + 0.02	2179.9 + 0.1	2456.3 + 0.2		
3734.51	3768.91 + 0.04		2449.2 + 0.4		
3722.08	[3756.24] ...		2443.7 + 0.3		
3712.11			2439.2 + 0.4		

Although the method of computation scarcely needs an explanation, I will nevertheless illustrate it by one example. Suppose we want to find the 3rd helium-line (from the top). The corresponding H-line is $l = 4340.63$, further $\lambda_x = 3756.24$ and $l_x = 3722.08$, hence

$$\frac{1}{\lambda - 3756.24} = \frac{\alpha_5}{4340.63 - 3722.08} + \beta_5 = 0.0015859 - 0.0000032 = 0.0015827$$

$$= 3756.24 + 631.83 = 4388.07.$$

The existence of so remarkable a relation between the line-series of different elements is a novel and certainly important feature, the discovery of which we owe to the application of the RYDBERG-THIELE formula. In some cases the relation

between series belonging to different chemical atoms is still closer. If we write our original equation (2) in the form

$$\frac{1}{\nu_{\infty} - \nu} = a_1[(m + \mu)^2 \pm c^2], \quad c^2 = \frac{b_1}{a_1} \quad (9)$$

we find that in certain cases the expression within the brackets is the same for two series. Under this special condition we have obviously

$$\frac{\nu_{\infty} - \nu}{n_{\infty} - n} = \text{const.}$$

I have found the following four instances of this kind :

(1) Zinc, 1st S.S., and Indium, 1st S.S. Calling the difference $(\nu_{\infty} - \nu)$ in the case of Zn : $[\nu]_{Zn}$ and in the case of In : $[\nu]_{In}$ we find from the preceding tables

$[\nu]_{Zn}$	$[\nu]_{In}$	$0.94374[\nu]_{In}$
13029	13807	13030
7217	7647	7217
4585	4860	4587
3173	3357	3168
2326	2471	2332
1779	1882	1776

Hence we have, with sufficient accuracy : $[\nu]_{Zn} = 0.94374[\nu]_{In}$.

(2) Zinc, 1st S.S., and Mercury, 1st S.S.

$[\nu]_{Zn}$	$[\nu]_{Hg}$	$1.01137[\nu]_{Hg}$
13029	12884	13031
7217	7134	7215
4585	4537	4588
3173	3134	3170

It obviously follows that $[\nu]_{Zn} = 0.94374[\nu]_{In} = 1.01137[\nu]_{Hg}$.

(3) Zinc, 2nd S.S., and Mercury, 2nd S.S.

$[\nu]_{Zn}$	$[\nu]_{Hg}$	$1.01286[\nu]_{Hg}$
22138	21856	22138
10374	10243	10374
6061	5986	6063
3985	3934	3985
2824	2788	2824

(4) Lithium, 1st S.S., and Hydrogen, 1st S.S.

$[\nu]_{Li}$	$[\nu]_H$	$1.00177[\nu]_H$
12211	12189	12211
6867	6856	6868
4396	4388	4395
3053	3047	3052
2243	2238	2242
1705	1714	1717
1351	1354	1356

The RYDBERG-THIELE equation in the form given in (9) presents some striking regularities of the constants which deserve to be mentioned. If we consider first the cases (by far the most frequent) where b_1 is negative, we may write the equation in the form :

$$[\nu_\infty - \nu]^{-1} = a_1(m + \mu + c)(m + \mu - c) = a_1(m + d)(m + e) \quad (10)$$

Now it appears that in a certain group of elements, such for instance as the alkalis, the constants d and e may be represented by common fractions having the same denominator. Thus we find for the subsidiary series the following numerical equations :

Li	1. S.S. :	$[\nu_\infty - \nu]^{-1} = [4.95899 - 10]m \cdot m$	$\nu_\infty = 28595$
	2. S.S. :	$= [4.96101 - 10](m - \frac{3}{15})(m - \frac{3}{15})$	$= 28580$
Na	1. S.S. :	$= [4.95748 - 10](m + \frac{2}{15})(m - \frac{2}{15})$	$= 24481$
	2. S.S. :	$= [4.95512 - 10](m + \frac{3}{15})(m - \frac{1}{15})$	$= 24481$
K	1. S.S. :	$= [4.94046 - 10](m + \frac{1}{15})(m - \frac{1}{15})$	$= 22049$
	2. S.S. :	$= [4.92668 - 10](m + \frac{1}{15})(m - \frac{1}{15})$	$= 22005$
Rb	1. S.S. :	$= [4.90881 - 10](m + \frac{1}{15})(m - \frac{1}{15})$	$= 21202$
Cs	S.S. :	$= [4.90432 - 10](m + \frac{2}{15})(m - \frac{2}{15})$	$= 19746$

The coefficients a_1 are given as logarithms. The wave-frequencies computed by means of these equations leave the following errors in the observations :

Li_1	Li_2	Na_1	Na_2	K_1	K_2	Rb	Cs
0	+ 2	0	0	+ 1	+ 1	+ 1	+ 2
+ 2	- 1	- 1	0	- 3	0	- 2	- 7
0	0	0	+ 1	0	+ 2	+ 3	- 2
0	+ 1	0	0	+ 2	+ 3	+ 1	+ 2
- 1	- 13	- 8	+ 3	- 2	0	- 1	+ 1
+ 12		+ 3	+ 10	- 1	- 16	- 2	0
+ 6		- 1		- 8	- 10		+ 1
							+ 3

These errors are sufficiently small to be explained by the uncertainties of the measurements; they are indeed of the same order as those previously met with and considerably less than the corresponding residuals of KAYSER's equation. Turning to

the principal series we find that here also the denominator 15 plays an important part. Thus, considering the first components, the values of c are for Li: 0.199, for Na: 0.548, for K: 0.805, for Rb: 1.083, and for Cs: 1.328, hence very nearly $\frac{3}{15}$, $\frac{8}{15}$, $\frac{12}{15}$, $\frac{16}{15}$ and $\frac{20}{15}$. Except Li, the values of c and μ form an arithmetic progression. For we notice that μ is represented by the fractions $-\frac{1}{20}$, $\frac{4}{20}$, $\frac{8}{20}$, $\frac{12}{20}$, $\frac{16}{20}$, the numerators of which are obtained from those of the quantities c by subtracting 4. Such regularities cannot be accidental, although we must confess that at present it is impossible to assign a meaning to them. Nor are they confined to the group of elements here considered. Thus we may easily convince ourselves that, for instance, the four series of Oxygen mentioned before are represented by the equations:

1. Triplet:	$(\nu_{\infty} - \nu)^{-1} = [4.95404 - 10][m^2 - (\frac{4}{15})^2]$	$\nu_{\infty} = 23212.5$
2. Triplet:	$= [4.95750 - 10][(m - \frac{3}{15})^2 - (\frac{6}{15})^2]$	23207.3
1. Pair:	$= [4.96523 - 10][(m - \frac{3}{15})^2 + (\frac{6}{15})^2]$	21201.7
2. Pair:	$= [4.95587 - 10][m^2 - (\frac{3}{15})^2]$	21212.7

Similar conditions we find in three of the six Helium-series, viz.,

1st P.S.:	$[\nu_{\infty} - \nu]^{-1} = [4.95884 - 10][(m - \frac{1}{15})^2 + (\frac{2}{15})^2]$	$\nu_{\infty} = 38466.8$
1st S.S.:	$= [4.95913 - 10][m^2 - (\frac{1}{15})^2]$	29231.6
3d S.S.:	$= [4.95930 - 10][m^2 - (\frac{1}{15})^2]$	27182.4

whereas in the other three series the fractions contain the denominator 2×15 , viz.,

2nd P.S.:	$[\nu_{\infty} - \nu]^{-1} = [4.96161 - 10][m^2 + (\frac{5}{30})^2]$	$\nu_{\infty} = 32036.9$
2nd S.S.:	$= [4.96066 - 10][(m - \frac{9}{30})^2 - (\frac{5}{30})^2]$	29229.2
4th S.S.:	$= [4.95943 - 10][(m - \frac{4}{30})^2 - (\frac{7}{30})^2]$	27181.4

The series of the three elements Mg, Ca and Sr, on the other hand, appear to be well represented by fractions with the denominator 14. I have found the following numerical equations:

Mg	1st S.S.:	$[\nu_{\infty} - \nu]^{-1} = [4.95105 - 10](m + \frac{5}{14})(m - \frac{8}{14})$	$\nu_{\infty} = 39781$
	2nd S.S.:	$= [4.94696 - 10](m + \frac{13}{14})(m - \frac{5}{14})$	39779
Ca	1st S.S.:	$= [4.95797 - 10](m + \frac{15}{14})(m - \frac{9}{14})$	34067
	2nd S.S.:	$= [4.94622 - 10](m + \frac{23}{14})(m - \frac{4}{14})$	34005
Sr	1st S.S.:	$= [4.93097 - 10](m + \frac{25}{14})(m - \frac{11}{14})$	31636
	2nd S.S.:	$= [4.92352 - 10](m + \frac{33}{14})(m - \frac{5}{14})$	31079

All these regularities seem to me interesting enough to be mentioned in this discussion, although I admit that without a theoretical foundation they are perhaps of but little importance. Nevertheless the mere fact that the RYDBERG-THIELE equation is capable of showing so many interesting links between the series of different chemical elements, of which we see no traces in other formulæ, speaks highly in its favour, especially if considered in conjunction with the no longer doubtful property of this formula, that it satisfies the observations much better than other empirical equations hitherto proposed. But the chief importance of the RYDBERG-THIELE formula seems to me to lie in some other properties which we are now to discuss.

It may be shown that an interesting geometrical relation exists between the line-series belonging to the same μ -group. If, in fig. 1, the points $a_1, a_2 \dots a_m$, are fixed upon the straight line AB so that the distance $Aa_m = (m + \mu)^2$, and if from any point O outside this line we draw the straight paths $Ov_0, Ov_1, Ov_2 \dots Ov_m \dots Ov_\infty$, through A, $a_1, a_2 \dots a_m \dots a_\infty$, any line-series belonging to this particular group, which has been arranged along a transversal line CD so that the distance between consecutive points corresponds, on some arbitrary scale, to the differences of the wave-frequencies of consecutive lines, can be placed in such a position that all

FIG. 1.

the spectral lines fall exactly upon the rays $Ov_0, Ov_1, Ov_2 \dots$. The proof of this theorem is very simple. If the dotted line, CE, be drawn parallel to AB, we have :

$$Cb_1 = \frac{CO}{AO} \cdot Aa_1$$

$$Cb_2 = \frac{CO}{AO} \cdot Aa_2$$

.....

and generally

$$Cb_m = \frac{CO}{AO} \cdot Aa_m = \frac{CO}{AO} \cdot (m + \mu)^2.$$

Further we have from the similar triangles Cc_mb_m and Oc_mD :

$$\frac{Cc_m}{c_mD} = \frac{Cb_m}{OD} = \frac{CO}{AO \cdot OD} \cdot (m + \mu)^2.$$

On the other hand, from the RYDBERG-THIELE formula (3)

$$\frac{\nu_m - \nu_0}{\nu_\infty - \nu_m} = \alpha_2(m + \mu)^2.$$

Hence, if the transversal CD be drawn in such a manner that

$$\frac{CO}{AO \cdot OD} = \alpha_2,$$

we find

$$\begin{aligned} (c_m = \nu_m - \nu_0 \quad \text{and} \quad c_m D = \nu_\infty - \nu_m, \quad \text{and hence} \\ c_1 c_2 = \nu_2 - \nu_1, \quad c_2 c_3 = \nu_3 - \nu_2, \quad \dots \quad CD = \nu_\infty - \nu_0) \end{aligned} \quad Q.E.D.$$

If, now, all the series belonging to the same μ -group be arranged in our diagram, in every case the lines could be made to fall upon the rays $Or_0, Or_1, \dots, Or_\infty$, so that

FIG. 2.

to an observer stationed at O all these series would seem to coalesce into one. In virtue of equation (4) the same geometrical property holds good, if we consider wave-lengths instead of wave-frequencies.

From the above theorem we deduce at once the following corollary :

If we fix upon a straight line, on any arbitrary scale, the lines of a given series in such a way that the distances between two lines express the differences of the corresponding wave lengths or frequencies, and if from any point outside we draw straight paths through these spectral lines, then the lines of any other series belonging to the same μ -group can be represented as the points of intersection of these straight paths with a certain transversal line.

An illustration of this geometrical relation is given in fig. 2 for some series

belonging to the group $\mu = 0$. On the lowest horizontal line the wave-lengths of the first Hydrogen-series (BALMER's formula) have been drawn on a certain scale (in the original drawing 10 t.m. = 1 mm.), beginning with $m = 3$ ($\lambda_3 = 6563.07$) on the left to $m = \infty$ ($\lambda_\infty = 3646.10$) on the right. The points 3, 4, 5, . . . thus obtained were then connected with a point O arbitrarily fixed in the plane of the paper. If now we draw, not necessarily but for the sake of convenience, on the *same* scale, the wave-lengths of, say, the 1st subsidiary series of Lithium on another straight line, for instance the edge of a ruler, we can bring this line on our diagram into such a position that its intersections with the rays $O_3, O_4, \dots O_\infty$ mark precisely the positions of all the lines of the series. The line is indicated in the drawing by the transversal Li. In the same way the transversals He, Tl, Zn and In represent the 2nd principal series of Helium and the 1st subsidiary series of Thallium, Zinc and Indium, which, as we have seen before, belong to this particular group $\mu = 0$. Obviously the "tails" of all these series are situated upon the ray O_∞ , while the "heads" lie upon O_0 which corresponds to $m = 0$. In line-series these "heads" are of no special interest, because they correspond to wave-lengths outside the range of observation. Nevertheless, they will be considered here on account of their great importance in relation to our investigation of the band-spectra in subsequent pages. The construction of fig. 2 was based on wave-lengths in order to show that the RYDBERG-THIELE formula may also be employed in the form given by equation (4). For theoretical purposes, however, an investigation founded on wave-frequencies must doubtless be preferred. This has been already pointed out by RYDBERG, KAYSER, SCHUSTER and others. We shall therefore now revert to our formulæ referring to wave-frequencies.

Since the position of O is quite arbitrary, we may conveniently choose it so that the two boundary rays $O\nu_0$ and $O\nu_\infty$ form a right angle. In this case the cotangent of the angle α between the rays $O\nu$ and $O\nu_\infty$ (fig. 3) is equal to $(m + \mu)^2$, if we make $AO = 1$. Let us further call β the angle formed by the ray $O\nu_0$ and the transversal which represents our series. Since $cc_\infty = \nu_\infty - \nu$ and $\angle Occ_\infty = 90^\circ - \alpha - \beta$, we have from triangle Occ_∞ :

$$\nu_\infty - \nu = Oc_\infty \cdot \frac{\sin \alpha}{\cos (\alpha + \beta)} = a_\infty \cdot \frac{\sin \alpha}{\cos (\alpha + \beta)}. \quad (11a)$$

On the other hand, from triangle Occ_0 we find

$$\nu - \nu_0 = Oc_0 \cdot \frac{\cos \alpha}{\cos (\alpha + \beta)} = a_0 \cdot \frac{\cos \alpha}{\cos (\alpha + \beta)}. \quad (11b)$$

Comparing the first of these formulæ with equation (2) we see at once that

$$Oc_\infty = \frac{\cos \beta}{a_1} = a_\infty$$

$$\tan \beta = -\frac{b_1}{a_1}$$

The RYDBERG-THIELE equation may therefore be written in the form

$$\nu = \nu_\infty - a_\infty \cdot \frac{\sin \alpha}{\cos (\alpha + \beta)}. \quad (12)$$

This is probably the most convenient form for computation. It becomes identical with BALMER's formula for $\mu = 0$ and $\beta = 0$, because we have then $\tan \alpha = m^{-2}$ and

$$v = v_x - a_x \cdot \tan \alpha = v_c - a_x \cdot m^{-2}.$$

If only $\beta = 0$, we find RYDBERG's formula

$$\nu = \nu_{\infty} - a_{\infty} \cdot (m + \mu)^{-2}.$$

Hence we see that both BALMER's and RYDBERG's equations suppose the transversal to be parallel to the ray $0\nu_0$, whereas, according to the more general RYDBERG-THIELE formula, the two lines may form any angle β with each other.

Now, an important result is arrived at if we investigate more closely these angles β . We notice that while in some cases β is small, and hence the transversals are nearly parallel to $0\nu_0$, there are also instances where this angle is considerable. The extreme case

FIG. 3.

seems to be represented by Cæsium, where β is about 64° . Naturally the question arises, what would happen if β should become still greater and should finally be $\pm 90^\circ$. In this case the transversal representing our series would be parallel to the ray $O\nu_\infty$, and hence a_∞ would become infinite. But from the equation (11*b*) we find that

$$\nu = \nu_0 \mp \alpha_0(m + \mu)^2. \quad (13)$$

Now obviously this equation is a more general form of DESLANDRES' formula for the *band-spectra* into which it converges for $\mu = 0$, viz.

$$\nu = \nu_0 \mp a_0 m^2,$$

where ν_0 represents the wave-frequency of the *first* line (the “head” of the band), while the upper or the lower sign indicates that the band “shades off” towards the red or the violet side respectively. We perceive, then, that the RYDBERG-THIELE formula includes as a special case also the DESLANDRES formula, and thus opens the prospect of

the two phenomena, the line- and band-series, being comprised under one and the same mathematical, and probably also physical, conception.

From what has been found in the case of the line-spectra it appears now extremely probable that DESLANDRES' formula represents only a limited number of band-spectra and is but a special case of our more general equation, just as BALMER's formula is a particular instance of the same equation in the case of line-spectra. A considerable part of the remainder of the present communication will be devoted to the investigation of this point. Before entering upon this new side of the question, however, I should like to discuss briefly, for the convenience of those readers who are interested in the foregoing computations, a method by which the four constants of the RYDBERG-THIELE formula may be determined from one of the two equations (5). If $\nu_x, \nu_y, \nu_z, \nu_w$ are the wave-frequencies of any four lines of the series, we have from the second of (5) :

$$\frac{1}{\nu_z - \nu_x} = \frac{a_3}{(z + \mu)^2 - (x + \mu)^2} + b_3 = \frac{a_3}{(z + x + 2\mu)(z - x)} + b_3 \quad (a)$$

$$\frac{1}{\nu_y - \nu_z} = \frac{a_3}{(y + x + 2\mu)(y - x)} + b_3 \quad (b)$$

$$\frac{1}{\nu_w - \nu_y} = \frac{a_3}{(w + y + 2\mu)(w - y)} + b_3 \quad (c)$$

$$\frac{1}{\nu_w - \nu_z} = \frac{a_3}{(w + z + 2\mu)(w - z)} + b_3 \quad (d)$$

Subtracting (c) from (a) and (d) from (b), and dividing, we obtain after slight transformations :

$$\frac{(x + y + 2\mu)(z + w + 2\mu)}{(x + z + 2\mu)(y + w + 2\mu)} = \frac{(z - x)(w - y)}{(y - x)(w - z)} \cdot \frac{(\nu_y - \nu_z)(\nu_w - \nu_x)}{(\nu_z - \nu_x)(\nu_w - \nu_y)} = c, \text{ say,} \quad (e)$$

or by substituting

$$y - x = p$$

$$z - x = q$$

$$w - x = r$$

$$\frac{[p + 2(\mu + x)][q + r + 2(\mu + x)]}{[q + 2(\mu + x)][p + r + 2(\mu + x)]} = c, \text{ and}$$

$$(\mu + x)^2 + \frac{p + q + r}{2}(\mu + x) + \frac{p(q + r) - q(p + r)c}{4(1 - c)} = 0.$$

The positive root of this quadratic equation is the desired value of $(\mu + x)$. Let us take as an example the principal series of Sodium and select the 1st, 3rd, 5th, and 7th observed line for our computation. From the observations we have therefore :

$$\begin{array}{lll} \nu_x & = 16960.19 & z - x = 4 \quad p = 2 \\ \nu_y = \nu_{x+2} & = 35051.93 & w - y = 4 \quad q = 4 \\ \nu_z = \nu_{x+4} & = 38550.80 & y - x = 2 \quad r = 6 \\ \nu_w = \nu_{x+6} & = 39805.27 & w - z = 2 \end{array}$$

$$c = \frac{4 \cdot 4}{2 \cdot 2} \times \frac{18091.74 \times 1254.47}{21590.61 \times 4753.34} = 0.884582$$

$$(\mu + x)^2 + 6(\mu + x) - 17.992 = 0; \mu + x = 2.195.$$

The remaining computations are now simple. We have

$$\frac{1}{\nu_y - \nu_x} = \frac{1}{18091.74} = \frac{a_3}{(4.195)^2 - (2.195)^2} + b_3$$

$$\frac{1}{\nu_z - \nu_x} = \frac{1}{21590.61} = \frac{a_3}{(6.195)^2 - (2.195)^2} + b_3,$$

and hence

$$\log a_3 = 6.26686 - 10$$

$$\log b_3 = 5.61075 - 10.$$

But from (5) and (2) we find

$$b_3 = \frac{1}{\nu_\infty - \nu_x}; \quad a_1 = \frac{b_3^2}{a_3}; \quad \frac{1}{\nu_0 - \nu_x} = -\frac{a_3}{(2.195)^2} + b_3.$$

And finally from these relations:

$$\log a_1 = 4.95464 - 10; \quad \log b_1 = 4.41367_n - 10; \quad \nu_\infty = 41464.9.$$

These constants differ slightly from those previously computed under the assumption that $x + \mu = 2.200$, but they represent the observations almost equally well.

It may be remarked that the relation (e) can also be derived from a well-known geometrical theorem. If, in fig. 1, we take any four points a_x, a_y, a_z and a_w on the line AB and the four corresponding points c_x, c_y, c_z and c_w on the transversal CD, so that a_x and c_x lie on the same ray $O\nu_x$, a_y and c_y on the ray $O\nu_y$, etc., then we know from geometry that

$$\frac{a_x a_y}{a_x a_z} \cdot \frac{a_z a_w}{a_y a_w} = \frac{c_x c_y}{c_x c_z} \cdot \frac{c_z c_w}{c_y c_w}.$$

But we remember that $a_x a_y = (y + \mu)^2 - (x + \mu)^2$ and $c_x c_y = \nu_y - \nu_x$ etc., so that

$$\frac{\nu_y - \nu_x}{\nu_z - \nu_x} \cdot \frac{\nu_w - \nu_z}{\nu_w - \nu_y} = \frac{(y + \mu)^2 - (x + \mu)^2}{(z + \mu)^2 - (x + \mu)^2} \cdot \frac{(w + \mu)^2 - (z + \mu)^2}{(w + \mu)^2 - (y + \mu)^2}, \quad \text{or}$$

$$\frac{(z - x)(w - y)}{(y - x)(w - z)} \cdot \frac{(\nu_y - \nu_z)(\nu_w - \nu_z)}{(\nu_z - \nu_x)(\nu_w - \nu_y)} = \frac{(x + y + 2\mu)(z + w + 2\mu)}{(x + z + 2\mu)(y + w + 2\mu)},$$

which is identical with (e).

B. BAND-SPECTRA.

The fact that the RYDBERG-THIELE equation represents both line- and band-series is perhaps most strikingly demonstrated by the following computations where the wave-lengths of the lines of the Cyanogen-band (see KAYSER, *Handbuch*, vol. ii. p. 479) are used for determining the wave-lengths of the first triplet series of Oxygen given on p. 564. If in equation (8)

$$\frac{1}{\lambda - \lambda_x} = \frac{\alpha_5}{l - l_x} + \beta_5$$

we take for l successively the wave-lengths of the 40th, 50th, etc., line of the Cyanogen-band, l_x being the wave-length for the 100th line for instance, and if we further make

$$\log \alpha_5 = 9.60800 - 10$$

$$\log \beta_5 = 7.63969_n - 10,$$

we obtain the values $(\lambda - \lambda_x)$ shown in the third column of the following table :

1	2	3	4	5	6
Cyanogen-band.	$l - l_x$	$\lambda - \lambda_x$	λ	1st Triplet Series of Oxygen (1st Comp.).	Difference Obs. - Comp.
$l_{40} = 3866.95$	81.53	1634.70	6158.41	6158.41	0.00
$l_{50} = 3857.82$	72.40	807.14	5330.84	5330.84	0.00
$l_{60} = 3846.79$	61.37	445.31	4969.01	4968.94	- 0.07
$l_{70} = 3833.93$	48.51	250.18	4773.88	4773.94	+ 0.06
$l_{80} = 3819.36$	33.94	131.83	4655.53	4655.54	+ 0.01
$l_{90} = 3803.16$	17.74	54.07	4577.77	4577.84	+ 0.07
$l_{100} = 3785.42$	0.00	0.00	4523.70	4523.70	...

Adding to each figure of column 3 the constant 4523.70 we find the values of λ in column 4. The 5th column, on the other hand, contains the observed wave-lengths of the first triplet series (1st component) of Oxygen according to the measurements by RUNGE and PASCHEN (see p. 564). The very close agreement between 4 and 5 shows conclusively that the RYDBERG-THIELE equation satisfies the conditions of both series. Instead of the Oxygen-series we might, of course, have selected any series of the group $\mu = 0$.

In my introductory remarks I have alluded to Professor THIELE's investigation of the third band of the Carbon-spectrum (*Astrophysical Journal*, vol. viii. p. 1). I have mentioned that Professor THIELE found himself obliged to reject the simple formula here used, although he had been the first to notice some of its remarkable properties. His contention, however, that the formula does not sufficiently satisfy the observations, is not acceptable, as will be conclusively shown in the computations which follow. Indeed, if we study more closely the conditions under which Professor THIELE made use of the formula, we come to the conclusion that his negative result is due not so much to a deficiency in the equation employed, as to a particular extra demand imposed upon it. For Professor THIELE introduces an assumption which, though it may have some mathematical probability, has certainly so far no physical foundation. He assumes that all the series of the band should appear coupled in pairs, and that each pair should be represented by one and the same equation, the two branches being obtained by assigning to m either its positive or negative value. This hypothesis necessitates equations of great complexity, involving at least eight constants. It must appear difficult, if not altogether impracticable, to use cumbersome formulæ such as those obtained by Professor THIELE as a basis for theoretical investigations, nor are they of use as purely empirical expressions of the law of the spectral structures. But this complexity disappears as soon as we abandon Mr THIELE's assumption. If we consider by itself each of the many series which he has so successfully unravelled by his masterly treatment of the Carbon-band here considered, we

find that the RYDBERG-THIELE formula satisfies the observations well within their mean errors, the agreement being on the whole even closer than in Professor THIELE's computations. I have carried out the necessary computations for ten series, viz., for the five pairs $\alpha\pm$, $\beta\pm$, $\gamma\pm$, $\delta\pm$, and $\epsilon\pm$, but will present here, for the sake of brevity, only the results of the first two pairs. Since Professor THIELE employed wave-lengths in his calculations, I follow his example and use the second of equations (6):

$$\frac{1}{\lambda_0 - \lambda} = \frac{a_1}{(m + \mu)^2} + \beta_1 = \frac{a_4}{(m + \mu)^2} + \frac{1}{\lambda_0 - \lambda_\infty}$$

Series:	$\log a_4$	λ_0	λ_∞
$\alpha +$	0.87883	5165.10	2241.1
$\alpha -$	0.88016	5165.10	2188.5
$\beta +$	0.87840	5165.18	2271.6
$\beta -$	0.87973	5165.18	2219.0

In the following comparisons I give now the results for every fifth line of the series:

$\alpha + ; (m + \mu)$	λ obs.	λ comp.	O. - C.	$\alpha - ; (m + \mu)$	λ obs.	λ comp.	O. - C.
5.0	5161.77	.81	-.04	4.5	5162.41	.43	-.02
10.0	5151.87	.94	-.07	9.5	5153.21	.26	-.05
15.0	5135.63	.66	-.03	14.5	5137.62	.65	-.03
20.0	5113.17	.17	.00	19.5	5115.84	.82	+.02
25.0	5084.80	.76	+.04	24.5	5088.11	.05	+.06
30.0	5050.86	.79	+.07	29.5	5054.73	.68	+.05
35.0	5011.66	.67	-.01	34.5	5016.12	.10	+.02
40.0	4967.84	.87	-.03	39.5	4972.78	.78	.00
				45.5	4915.16	.20	-.04

$\beta + ; (m + \mu)$	λ obs.	λ comp.	O. - C.	$\beta - ; (m + \mu)$	λ obs.	λ comp.	O. - C.
5.0	5161.95	.88	+.07	4.5	5162.60	.51	+.09
10.0	5151.97	2.01	-.04	9.5	5153.32	.32	.00
15.0	5135.70	.71	.01	14.5	5137.72	.71	+.01
20.0	5113.17	.21	-.04	19.5	5115.84	.86	-.02
25.0	5084.80	.78	+.02	24.5	5088.11	.07	+.04
30.0	5050.86	.81	+.05	29.5	5054.73	.69	+.04
35.0	5011.66	.69	-.03	34.5	5016.12	.12	.00
40.0	4967.84	.92	-.08	39.5	4972.78	.81	-.03

We notice that all the four series possess "tails," a result which has already been obtained by Professor THIELE. Geometrically speaking, this means that the transversal representing the series is *not* parallel to the ray $O\nu_\infty$, but intersects this line at a certain point. We shall see that this is a general feature of the band-series.

In the *Astrophysical Journal*, vol. xx. No. 2, Mr LESTER has recently published most accurate measurements of the telluric Oxygen-bands of the solar spectrum. We shall proceed to investigate how far his observations are accounted for by the RYDBERG-THIELE formula. The general structure of the groups A, B, α and α' , may be described as follows. Each group consists of two series of doublets called by Mr LESTER the first and second band, in each of which he distinguishes the two components as the first and second series. In the following tables I exhibit the results of my computations made on some of the series of the three groups A, B, and α .

OXYGEN-BAND. A group. First Band. First Series.

$$\log \alpha_4 = 0.70266_n$$

$$\log b_4 = 6.57928_n - 10$$

$$\lambda_0 = 13168.40$$

B Group. First Band. First Series.

$$\log \alpha_4 = 0.90992_n$$

$$\log \beta_5 = 6.68740 - 10$$

$$\lambda_0 = 6867.379$$

$(m + \mu)$	ν obs.	ν comp.	Obs. - Comp.	$(m + \mu)$	λ obs.	λ comp.	Obs. - Comp.
0.75	13168.29	.29	.00	0.8	6867.458	.458	.000
1.75	13167.81	.80	+ .01	1.8	67.794	.778	+ .016
2.75	13166.89	.90	- .01	2.8	68.337	.344	- .007
3.75	13165.61	.61	.00	3.8	69.144	.157	- .013
4.75	13163.94	.93	+ .01	4.8	70.220	.218	+ .002
5.75	13161.88	.86	+ .02	5.8	71.528	.527	+ .001
6.75	13159.39	.40	- .01	6.8	73.078	.085	- .007
7.75	13156.51	.54	- .03	7.8	74.888	.893	- .005
8.75	13153.30	.30	.00	8.8	76.953	.952	+ .001
9.75	13149.69	.68	+ .01	9.8	79.275	.266	+ .009
10.75	13145.70	.68	+ .02	10.8	81.80	.83	- .03
11.75	13141.36	.30	+ .06	11.8	84.65	.66	- .01
12.75	13136.58	.55	+ .03	12.8	87.75	.74	+ .01
13.75	13131.43	.43	.00	13.8	91.05	.08	- .03
				14.8	6894.67	.69	- .02

α Group. First Band. First Series.

$$\log \alpha_4 = 0.88746_n$$

$$\log \beta_4 = 7.25370 - 10$$

$$\lambda_0 = 6276.79$$

$(m + \mu)$	λ obs.	λ comp.	Obs. - Comp.
0.4	6276.81	.81	.00
1.4	77.03	.04	- .01
2.4	77.52	.54	- .02
3.4	78.29	.29	.00
4.4	79.31	.31	.00
5.4	80.61	.60	+ .01
6.4	82.16	.15	+ .01
7.4	84.00	3.98	+ .02
8.4	86.09	.09	.00
9.4	88.48	.48	.00
10.4	6291.14	.16	- .02

I must remark here that the determination of μ in band-spectra is a somewhat uncertain operation. In the first series, for instance, the fraction 0.8 might have been used

instead of 0.75 without sensibly altering the differences of the last column. In all cases the agreement between the observed and computed wave-lengths and wave-frequencies is doubtless sufficiently close to justify the assertion that the RYDBERG-THIELE formula represents the measurements most accurately. The same agreement is shown in the following calculations, which refer to some of the second bands.

B Group. Second Band. First Series.

$$\log \alpha_5 = 0.90992_n \quad \lambda_0 = 6867.379$$

$$\log \beta_5 = 6.68740 - 10$$

$(m + \mu)$	λ obs.	λ comp.	Obs. - Comp.
12.5	6886.004	.004	.000
13.5	89.183	.181	+ .002
14.5	92.614	.605	+ .009
15.5	96.282	.277	+ .005
16.5	6900.196	.196	.000
17.5	04.363	.366	- .003
18.5	08.785	.784	+ .001
19.5	13.449	.452	- .003
20.5	18.365	.371	- .006
21.5	23.542	.545	- .003
22.5	28.986	.970	+ .016
23.5	34.669	.649	+ .020
24.5	40.584	.584	.000
25.5	46.770	.771	- .001

B Group. Second Band. Second Series.

$$\log \alpha_4 = 0.57250_n \quad \nu_0 = 14558.57$$

$$\log \beta_4 = 5.89220_n - 10$$

$(m + \mu)$	ν obs.	ν comp.	Obs. - Comp.
11.0	14526.27	.27	.00
12.0	14520.15	.15	.00
13.0	14513.49	.50	- .01
14.0	14506.29	.33	- .04
15.0	14498.65	.64	+ .01
16.0	14490.42	.43	- .01
17.0	14481.70	.69	+ .01
18.0	14472.45	.45	.00
19.0	14462.72	.70	+ .02
20.0	14452.43	.41	+ .02
21.0	14441.67	.63	+ .04
22.0	14430.37	.35	+ .02
23.0	14418.53	.55	- .02
24.0	14406.26	.26	.00

 α Group. Second Band. First Series.

$$\log \alpha_4 = 0.88756_n \quad \lambda_0 = 6276.63$$

$$\log \beta_4 = 6.36303 - 10$$

$(m + \mu)$	λ obs.	λ comp.	Obs. - Comp.
10.0	6289.60	.62	- .02
11.0	6292.35	.36	- .01
12.0	6295.36	.37	- 0.1
13.0	6298.64	.64	.00
14.0	6302.18	.17	+ .01
15.0	6306.00	5.98	+ .02
16.0	6310.06	.05	+ .01
17.0	6314.40	.40	.00
18.0	6319.02	.01	+ .01
19.0	6323.92	.91	+ .01
20.0	6329.10	.08	+ .02
21.0	6334.55	.53	+ .02
22.0	6340.28	.25	+ .03
23.0	6346.27	.26	+ .01

I have purposely computed wave-frequencies in some cases and wave-lengths in others in order to show that the RYDBERG-THIELE equation may be used in the same form in

both cases. It is not the object of this communication to enter upon a discussion of the constants, but merely to show in a number of typical cases the extraordinary accuracy of our formula. I shall therefore not discuss the other series of the Oxygen-bands, and reserve this particular investigation for another paper. One point, however, in connection with the second bands seems to require special mention. It is noticed that in these bands the index $(m + \mu)$ of the first visible line is a comparatively high number. According to the formula other lines before the one which "apparently" forms the head or beginning should be possible, but these lines are in fact not present in the spectrum. Instances of such "missing" lines are by no means rare among the band-spectra. Bands with "hypothetical" heads have indeed already been pointed out by Professor THIELE in his investigation of the Hydrocarbon-band. It is interesting to find at least one similar occurrence also among the line-series. According to Professor KAYSER the first observed double line of the 2nd Subsidiary Series of Potassium should be preceded by a strong pair at $\lambda = 6985$, which, however, has not been observed. Professor KAYSER remarks that this is the only case among all the line-series where computed lines seem to be actually missing. I am inclined to think that we have here a (so far) unique instance of a line-series with a hypothetical head. Perhaps the lines are not altogether absent, but are too faint to be noticed. It is quite a common feature in band-spectra that the intensity, instead of changing gradually from line to line, sometimes falls off abruptly. This abnormal phenomenon usually occurs in the tails, but there is no reason why it should not also be possible near the heads. We shall have to return to this interesting feature later on when we consider the structure of the Cyanogen-band.

Mr LESTER shows that the measured wave-frequencies of the Oxygen-band can be represented by an equation

$$\nu = \nu_0 - am - bm^2.$$

He lays particular stress on the existence of a term depending on the *first* power of m . Evidently his formula is a first approximation to the RYDBERG-THIELE equation, which may be written :

$$\nu - \nu_0 = \frac{(m + \mu)^2}{a_4 \left(1 + \frac{b_4}{a_4}(m + \mu)^2\right)} = \frac{(m + \mu)^2}{a_4} - \frac{b_4}{a_4^2}(m + \mu)^4 + \frac{b_4^2}{a_4^3}(m + \mu)^6 \dots$$

and can therefore be brought to Mr LESTER's form if m be counted from the first *observed* line. Thus we find in the case of the second band (second series) of the B-group from the constants of the RYDBERG-THIELE equation :

$$\nu = 14526.27 - 5.86m - 0.2635m^2 \dots$$

whereas Mr LESTER has :

$$\nu = 14526.27 - 5.86m - 0.2611m^2.$$

The examples here given are in my opinion quite sufficient to demonstrate the applicability of the RYDBERG-THIELE formula to both line- and band-spectra. The difference between these two types is seen to be solely due to the difference in the constants of our

equation. Specially striking is the contrast between the values of a_1 , which for band-series is always very much smaller than for line-series.

Professor THIELE has pointed out that in a band-series, proceeding from the head towards the tail, the distances between consecutive lines should first increase and afterwards diminish, and therefore reach a maximum at a certain point between the head and the tail. If we differentiate the RYDBERG-THIELE equation

$$\frac{1}{\nu_\infty - \nu} = a_1(m + \mu)^2 + b_1$$

with regard to ν and m , we find

$$\begin{aligned} \frac{d\nu}{dm} &= \frac{2a_1(m + \mu)}{[a_1(m + \mu)^2 + b_1]^2} \\ \frac{d^2\nu}{dm^2} &= \frac{2a_1}{[a_1(m + \mu)^2 + b_1]^2} \left[1 - \frac{4a_1(m + \mu)^2}{a_1(m + \mu)^2 + b_1} \right]. \end{aligned}$$

Hence the particular point $m_x + \mu$, for which the distance is a maximum, is found from the equation

$$1 - \frac{4a_1(m_x + \mu)^2}{a_1(m_x + \mu)^2 + b_1} = 0; \quad (m_x + \mu)^2 = \frac{1}{3} \frac{b_1}{a_1}.$$

But from fig. 3 we know that $\frac{b_1}{a_1} = \tan^2 \beta$, hence

$$(m_x + \mu)^2 = \frac{1}{3} \tan^2 \beta.$$

We see at once that for a series, whose transversal is parallel to $O\nu_0$ (e.g. the first Hydrogen Series) the maximum distance is at $m_x + \mu = 0$, i.e. at the beginning (head of the series), since $\beta = 0$; whereas for a series whose transversal is parallel to $O\nu_\infty$ [band-series satisfying DESLANDRES' special equation], the maximum distance is at $m_x + \mu = \infty$ (tail of the series), since $\beta = \pm \frac{\pi}{2}$; but that in general it must be at a point between

the head and the tail of the series. Thus we find without difficulty that in the α -series of the Hydrocarbon-band (see p. 579) the greatest distance between consecutive lines occurs between the 85th and 86th line.

Quite recently an important paper has been published by Dr JUNGBLUTH in the *Astrophysical Journal*, vol. xx. No. 4, in which the author discusses his exquisite measurements of the lines of the Cyanogen-band. I take this opportunity, therefore, of applying the RYDBERG-THIELE formula to this very extensive band, which, as Professor KAYSER has shown in his *Handbuch*, p. 479, seemed particularly inaccessible to a satisfactory representation by empirical formulæ. Before the appearance of Dr JUNGBLUTH's paper I had already attempted to compute the wave-lengths of this band by means of the formula proposed in this paper. It was found that the RYDBERG-THIELE formula gave excellent results up to about the 80th line, that the agreement could still be called very satisfactory up to the 140th line, but that further on the discrepancies increased enormously, and showed the formula to be not applicable throughout the whole extent of Professor KAYSER's observations. The question therefore arises, whether the formula, which has done such excellent work in the

shorter band-series, fails to account for the phenomena if they extend over a wider interval. If this could be proved, the RYDBERG-THIELE equation would certainly lose much of its value from the theoretical point of view. But there is an alternative. It is quite possible that the Cyanogen-band discussed by Professor KAYSER is not one single series, but really consists of several distinct parts apparently joined together so as to give the appearance of one continuous series. We have seen in the case of the Oxygen-band that two series of the same band need not necessarily exhibit their lines right down to their common head. It was noticed that while the one series which starts from the head may almost suddenly drop off on the tail side, the second series may show the inverse phenomenon, viz. a sudden decrease of intensity on the head-side. The effect of this peculiar behaviour is that the second series forms apparently the tail of the first series. Now in the Oxygen-bands both series consist of pairs of lines, but the distances between the components of the first (or head-) series are considerably smaller than those of the second (or tail-) series. Besides, in the head-series the distances decrease slightly towards the tail, while in the tail-series they increase very rapidly. To show this I subjoin a table giving Mr LESTER's wave-lengths of the B-group.

First (Head-) Series.	Second (Tail-) Series.	First (Head-) Series.	Second (Tail-) Series.
6867.46 { 1.00		6884.65 { 0.89	6884.08 { 1.92
68.46 { 0.99		85.54 { 0.85	86.00 { 2.20
67.79 { 0.97		87.75 { 0.82	86.98 { 2.47
68.78 { 0.99		88.60 { 0.83	89.18 { 2.72
68.37 { 0.96		91.05 { 0.83	90.14 { 3.00
69.34 { 0.96		91.87 { 0.83	92.61 { 3.24
69.14 { 0.96		94.67 { 0.83	93.56 { 3.52
70.13 { 0.94		6895.50 { 0.83	96.28 { 3.77
70.22 { 0.93			97.20 { 4.03
71.18 { 0.90			6900.20 { 4.30
71.53 { 0.92			01.12 { 4.57
72.49 { 0.92			04.36 { 4.57
73.08 { 0.92			05.26 { 4.57
74.04 { 0.92			08.78 { 4.57
74.89 { 0.92			09.68 { 4.57
75.83 { 0.92			13.45 { 4.57
76.95 { 0.92			14.33 { 4.57
77.88 { 0.92			18.36 { 4.57
79.27 { 0.92			19.24 { 4.57
80.17 { 0.92			23.51 { 4.57
81.80 { 0.92			24.42 { 4.57
6882.72 { 0.92			6928.99 { 4.57

Now let us suppose for a moment that the distances between the components are very much smaller, perhaps $\frac{1}{10}$ th only of those actually observed. The effect is that the first series appears as a single-line band, while the second, with sufficient dispersion, may still show its double character. Near the point where the two series coalesce, we would then have the following wave-lengths of the centres of the lines :

Single Line Series.	Double Line Series.
6877.11	
6879.72	
6882.26	
6885.09	6885.04
6888.18	6888.08
6891.46	6891.36
6895.08	6894.92
	6898.70

Here a remarkable phenomenon will be noticed, viz. that the positions of the centres of the double lines in the second series agree very nearly with those of the single lines of the first series. This is not accidental, because the other groups show the same feature. We have, for instance, in the A-group : (LESTER, *l.c.*, pp. 88 and 92)

Single Line Series.	Double Line Series.
7615.87	
7619.04	
7622.49	7622.40
7626.14	7626.04
7630.04	7629.90
	7633.98
	

and for the α group : (*l.c.*, pp. 89 and 91)

Single Line Series.	Double Line Series.
6284.38	
6286.49	
6288.84	6288.77
(6291.48)	6291.38
	6294.26
	

We notice, then, that at the point where the second series begins the line of the first series falls between the components of the former, and if its intensity is still sufficiently great and the doubles close, the effect of superposition will be that the resulting line appears as a broadened single line. Hence the lines of the first series, which near the head are thin and sharply defined, will gradually widen out. But since the intensity of the first series declines rapidly, their vitiating effect will lessen, the further we

proceed towards the tail, so that finally only the double line series will survive. It is very probable that the interval between the double lines which in the above bands increases steadily, may in more extensive groups reach a maximum and then decrease again further towards the tail. Now the feature thus described seems indeed to agree closely with the phenomena observed in the Cyanogen-band according to Dr JUNGBLUTH. I may be allowed to quote the author's own remarks on this important point, *i.e.*, 241 :—"Following the series further, another peculiarity appears, which, strange to say, has not been heretofore observed, though it comes out distinctly in the first-order spectrum. The lines become gradually broader as they recede from the head, and each finally separates into two lines when it has reached a breadth of about 0.07 t.m. We have now *double lines* similar to those above and below the second head. As the series proceeds, the interval between components of the double lines increases to 0.09–0.1 t.m., and then decreases until the components unite again to form one line. The lines of all the observed series show this behaviour, so that in certain parts of the band structure, as for example above and below λ 3700, we have only double lines." He further remarks that this is "a noteworthy property and must be considered in forming any valid theory concerning the origin of spectra." The most remarkable feature seems to me to be the coincidence of the centres of the lines in both series at the point where the second series begins. In consequence of this agreement the band changes from the single line to the double line type steadily, *i.e.* without indication of an abrupt change in the positions of the lines, thus giving the impression of one continuous series. But in fact, as the Oxygen-bands show, the series consists of two separate branches. The reason why in the Oxygen-bands we see a marked discontinuity between the two series is obviously that the lines of the first series fade off too early, *i.e.* before the beginning of the second series. If the faint close doubles, which Mr LESTER calls the continuation of the first series, were more prominent, the appearance of the Oxygen-bands would agree with that of the Cyanogen-band, though the intervals between the components are here too great to produce the impression of widened single lines by the coalescence of the four superimposed components.

I think that this view explains sufficiently the peculiar behaviour of the lines pointed out by Dr JUNGBLUTH. It reveals also a hitherto unknown similarity in the structure of bands of different substances, which may have a bearing on the theoretical aspect of the problem. But what interests us most of all at present is the probability that the first part of the Cyanogen-series consisting of single lines differs essentially from the second part, the double-line series, just as the first series of the Oxygen-bands differs from the second. I am inclined to think that there is even a third branch containing the single lines near the tail, so that in fact each of the four series given by Dr JUNGBLUTH consists of three distinct parts, each of which satisfies a different numerical form of the RYDBERG-THIELE equation. The correctness of this view may appear from the following tables, where the three branches of "Series I.,"

which I shall call I_a , I_b and I_c , are discussed. For the series I_a and I_b the computations have been made on every fifth line, for I_c on every second.

1a.

$$\log \alpha_1 = 1.98171, \quad \lambda_0 = 3883.50, \quad \lambda_\infty = 2199.39.$$

1b (first component).

$$\log \alpha_1 = 1.93237, \quad \lambda_0 = 3876.56, \quad \lambda_\infty = 2708.35.$$

$(m + \mu)$	λ obs.	λ comp.	O. - C.	$(m + \mu)$	λ obs.	λ comp.	O. - C.
5.0	3883.25	.24	+ .01	70.0	3823.98	.98	.00
10.0	3882.44	.46	- .02	75.0	3816.33	.33	.00
15.0	3881.15	.16	- .01	80.0	3808.29	.27	+ .02
20.0	3879.33	.34	- .01	85.0	3799.82	.82	.00
25.0	3876.99	7.01	- .02	90.0	3791.01	.00	+ .01
30.0	3874.14	.16	- .02	95.0	3781.83	.82	+ .01
35.0	3870.80	.79	+ .01	100.0	3772.32	.32	.00
40.0	3866.94	.97	- .03	105.0	3762.52	.51	+ .01
45.0	3862.62	.64	- .02	110.0	3752.41	.41	.00
50.0	2857.81	.82	- .01	115.0	3742.04	.05	- .01
55.0	3852.53	.53	.00	120.0	3731.44	.45	- .01
60.0	3846.79	.77	+ .02	125.0	3720.61	.62	- .01
65.0	3840.59	.56	+ .03	130.0	3709.63	.60	+ .03
70.0	3833.95	.90	+ .05	135.0	3698.50	.40	+ .10
74.0	3828.32	.26	+ .06				

1c.

$$\log \alpha_4 = 1.53310, \quad \lambda_0 = 3777.78, \quad \lambda_\infty = 3368.78.$$

$(m + \mu)$	λ obs.	λ comp.	O. - C.
64.0	3685.01	4.99	+ .02
66.0	3680.51	.49	+ .02
68.0	3676.00	.00	.00
70.0	3671.49	.50	- .01
72.0	3667.00	.01	- .01
74.0	3662.52	.54	- .02
76.0	3658.05	.06	- .01
78.0	3653.62	.62	.00
80.0	3649.21	.20	+ .01
82.0	3644.83	.81	+ .02
84.0	3640.45	.44	+ .01

The smallness of the residuals in the last columns proves again the applicability of the RYDBERG-THIELE equation, if we admit the suggested subdivision of the series into three apparently coherent branches. With regard to the other series of the band mentioned by Dr JUNGBLUTH, analogous structures are apparent, but I have not yet found time to undertake the necessary computations.

In his paper Dr JUNGBLUTH suggests that the tails of the four series may probably be represented by four faint bands shading off towards the red at wave-lengths 3579, 3603, 3629 and 3658. This suggestion had been already made by Mr KING, who had first observed the peculiar shadings in question. For several reasons I doubt the correctness of this view, and rather incline to think that Mr KING's bands represent

the "heads" of an independent Cyanogen-band distinguished from the others by the fact that, like the Oxygen-bands, its components shade off towards the *red*. First we must admit that the appearance of the bands does not agree with what we should expect if they were "tails." On the plate accompanying Dr JUNGBLUTH's paper they by no means convey the impression of an "infinity" of lines, but appear to be composed of a limited number of lines at finite distances from each other. This feature is specially noticeable at $\lambda = 3603$ and 3629 , and certainly agrees better with the supposition of "heads." It is also noteworthy that none of the tails of the 1st series computed above by means of the RYDBERG-THIELE formula agrees with any of the four wave-lengths of Mr KING's bands. Our experiences with the formula cannot but give us now some confidence that the structure of the band should be at least very nearly represented by it. On the other hand, however, Dr JUNGBLUTH's view seems to be supported to a certain extent by two noteworthy relations between the wave-lengths of the four heads of the series and the supposed tails. He showed that if we form the differences between the wave-lengths of corresponding heads and tails, we find

$$\begin{array}{rcl} 3884 - 3579 = 305 & & 36 \\ 3872 - 3603 = 269 & & 36 \\ 3862 - 3629 = 233 & & 36 \\ 3855 - 3658 = 197 & & 36 \end{array}$$

It appears, then, that the lengths of the successive series form an arithmetical progression. Again, if we form the quotients

$$\begin{array}{rcl} 3884 & & \\ 3579 = 1.0852 & & 0.0105 \\ 3872 & & \\ 3603 = 1.0747 & & 0.0105 \\ 3862 & & \\ 3629 = 1.0642 & & 0.0103 \\ 3855 & & \\ 3658 = 1.0539 & & \end{array}$$

we notice that these quotients also form approximately an arithmetical progression. Hence a somewhat remarkable connection seems indeed to exist between the observed heads and the alleged tails. But on a closer view this connection is found to be only apparent. For it is seen that the same relations exist, if we combine Mr KING's "tails" with the successive heads of the other Cyanogen-bands. Thus we find:

$$\begin{array}{rclclcl} 4606 - 3579 = 1027 & 52 & 4216 - 3579 = 637 & 43 & 3590 - 3579 = +11 & 28 \\ 4578 - 3603 = 975 & 51 & 4197 - 3603 = 594 & 42 & 3586 - 3603 = -17 & \\ 4553 - 3629 = 924 & 50 & 4181 - 3629 = 552 & 42 & 3584 - 3629 = -45 & 28 \\ 4532 - 3658 = 874 & & 4168 - 3658 = 510 & 42 & & \end{array}$$

These figures show therefore that Dr JUNGBLUTH's relation indicates not a specific connection between Mr KING's bands and the band at $\lambda = 3884$ only, but a far more general correspondence between the former and all the bands of the Cyanogen-spectrum. One might perhaps conclude that Mr KING's shadings may represent the common tail of

all the Cyanogen-bands, but this conclusion is evidently negatived by the last series at $\lambda = 3590$ mentioned in the preceding table, where the edges of the corresponding heads and tails would then be turned towards each other, *i.e.* the lines would not be within the space between head and tail. We notice also that Dr JUNGBLUTH's relation applies as well to the differences between the heads of the four Cyanogen-bands when compared one with the other. Thus :

$$\begin{array}{rcl} 4606 - 4216 = 390 & & 4216 - 3884 = 332 \\ 4578 - 4197 = 381 & 9 & 4197 - 3872 = 325 \\ 4553 - 4181 = 372 & 9 & 4181 - 3862 = 319 \\ 4532 - 4168 = 364 & 8 & 4168 - 3855 = 313 \end{array} \quad \begin{array}{l} 7 \\ 6 \\ 6 \\ 6 \end{array}$$

The most probable conclusion would therefore be that the alleged relation constitutes a property of the "heads" of the bands, and that Mr KING's shadings should be considered as the edges of a new band of the Cyanogen-spectrum, and not as the tails of the band at $\lambda = 3884$.

In concluding this section of my investigations dealing with the band-spectra, I may point out another form of the RYDBERG-THIELE formula which, though somewhat more complicated in appearance, reveals well its significant structure. Using wave-lengths we may write the equation in the form

$$\lambda = \frac{\lambda_0}{1 \pm \left(\frac{n}{\gamma}\right)^2} + \frac{\lambda_\infty}{1 \pm \left(\frac{\gamma}{n}\right)^2}, \quad (14)$$

where n stands for $(m + \mu)$ and where γ denotes a constant. We notice without difficulty that for $\lambda_0 = 0$, *i.e.* when

$$\lambda = \frac{\lambda_\infty}{1 \pm \left(\frac{\gamma}{n}\right)^2}, \quad (15)$$

the formula becomes identical with RYDBERG's equation for line-spectra, which again, on the further supposition that n represents integers, assumes the well-known form of BALMER's equation. So far, it is true, the observations have shown no evidence of series to which the positive sign in the denominator is applicable. In other words, no line-series have yet been found progressing from the violet towards the red, *i.e.* having their heads on the violet, and their tails on the red side of the spectrum. But the present investigation points now to the possibility of such regularities, and may perhaps induce physicists to search for series of this character.

If, on the other hand, we suppose $\lambda_\infty = 0$, equation (14) assumes the form

$$\lambda = \frac{\lambda_0}{1 \pm \left(\frac{n}{\gamma}\right)^2}, \quad (16)$$

which becomes identical with DESLANDRES' formula for band-series, if we assign to n integer values. The positive sign expresses that the band shades off towards the violet,

and *vice versa*. In general, the wave-lengths of the lines of any line- or band-series appear to be made up by two terms, the one satisfying the RYDBERG formula (15) and the other the more general DESLANDRES equation (16). This interpretation of the RYDBERG-THIELE formula shows perhaps more concretely than any other the fundamental character of its structure, and also its importance as the universal expression of spectral regularities.

C. GENERAL CONCLUSIONS.

We are now prepared to enter upon the discussion of some results of a more general character. The geometrical property of the RYDBERG-THIELE formula, as already indicated, enables us to represent on one single diagram every possible line- or band-series as a transversal on which the successive lines of the series are indicated by the points of intersection with the rays $O\nu$. On fig. 4 accompanying this paper I have indicated the positions of these transversals for a limited number of cases. The construction of the diagram is made sufficiently clear by the explanations already given, and therefore requires little additional comment. After the rays O_0 and O_∞ had been constructed at right angles to each other, a line was drawn parallel to O_∞ , and, starting from its point of intersection with O_0 , the successive values of $(m + \mu)^2$, on a conveniently chosen scale, were measured off. Through O and the points thus obtained lines were then drawn which are marked at their ends in our figure by the corresponding values of $(m + \mu)$. Obviously, in order to obtain the true inclinations β of the transversals, the parallel should be drawn at unit distance from the ray O_∞ . It was found, however, that under this condition the diagram would occupy too much space to be conveniently reproduced here, and I therefore decided to draw the parallel at a distance of 10 units. Consequently the inclinations of the transversals in the figure, which we may call β_0 , are considerably smaller, the two angles being in the relation $\tan \beta_0 = \frac{1}{10} \tan \beta$. The rays $O_1, O_2, O_3 \dots$, which correspond to integral values of $(m + \mu)$, have been represented by slightly stronger lines. Now, in the lower part of the diagram we find nearly all the line-series of the group $\mu = 0$. The chemical elements to which the series belong are indicated at the two ends of the transversals, and, where not otherwise stated, the latter refer to the 1st subsidiary series. If on any of these transversals we measure off the distances between consecutive points of intersection, these distances will be found to be exactly proportional to the corresponding wave-frequencies of the series to which the transversal refers. In this arrangement, therefore, all the spectral lines lie precisely on the rays $O_1, O_2, \dots$ and all the tail-ends on the ray O_∞ . Hence, if we imagine these rays to be represented by thin pencils of light, we may at once obtain the exact arrangement of the lines in any of these series by interposing a plane screen in a direction parallel to the corresponding transversal, since the centres of the luminous dots on the screen must then mark the true relative positions of the lines in the spectrum. There would perhaps be no difficulty in constructing an apparatus for lecture-purposes by which the correctness of

the RYDBERG-THIELE formula could thus be experimentally demonstrated. Turning to the upper part of the diagram, we find the transversals exhibiting the arrangements of lines in all the principal series. A smaller scale has been adopted in this case in order to keep the drawing within convenient dimensions, but otherwise the lines have been constructed on exactly the same principle as before. With regard to the intensity of the lines it must be noted as a general rule that the lines are strongest near the head and gradually decrease in brightness towards the tail, and that this rule applies to line-series as well as to band-series. Lastly, four specimens of band-spectra are exhibited by the four transversals nearly parallel to the ray O_∞ . In these cases, however, the scale had to be considerably enlarged, since otherwise the transversals would have been too close to O_∞ . The four series belong to the group $\mu = 0$, and the drawing is so arranged that the points of intersection with the rays $O_1, O_2, O_3 \dots$ represent the 10th, 20th, 30th $\dots$ line of the band.

In his researches on the band-series M. DESLANDRES points out that the wave-frequencies of the lines of such a series are arranged in a manner similar to those of the sound-vibrations produced by an elastic transversely vibrating rod. Indeed we recognise without difficulty that the series of sound-vibrations are represented in our diagram by transversals parallel to O_∞ . For it is well known from the mathematical investigations of POISSON, SEEBECK and others, that the wave-frequencies of the stationary transverse oscillations in a vibrating rod, with the exception of the two lowest vibrations, can be expressed by the relation

$$\frac{\nu}{\nu_x} = \frac{(m + \mu)^2}{(x + \mu)^2},$$

where μ depends on certain conditions under which the vibrations take place. But this equation is obviously of the form

$$\frac{1}{\nu - \nu_x} = \frac{a}{(m + \mu)^2 - (x + \mu)^2}, \quad (17)$$

and therefore agrees with the first of (5), if we assume $\nu_\infty = \infty$, *i.e.* if the transversal is parallel to O_∞ . The remarkable analogy between the sound-vibrations of an elastic body and the light-vibrations of a radiating atom or molecule is at least suggestive. Is it not, for instance, conceivable that the latter are caused by "standing waves" in the elastic system of electrons which constitutes the atom? If it were possible to find an elastic body of such shape and internal conditions that its transverse vibrations would satisfy the equation

$$\frac{1}{\nu - \nu_x} = \frac{a}{(m + \mu)^2 - (x + \mu)^2} + b, \quad (18)$$

where b is a constant, instead of the simpler relation (17), which refers to the special conditions in a uniform rod, the series of transverse sound-vibrations emitted by such a body would be exactly analogous to the series of light-vibrations emitted by the radiating atoms of a gas or vapour. We could then, by varying the conditions on which b depends, represent the acoustic analogies to the whole range of spectral phenomena

from the band-series to the line-series. At present we are, of course, ignorant of the conditions which lead to the more general equation (18), but at least this remarkable and highly suggestive feature has been brought out by our investigation, that the addition of a single constant to equation (17), the acoustic theory of which is well established, leads to the RYDBERG-THIELE formula, which, as we have demonstrated in the preceding sections, represents so completely all the phenomena of spectral regularities.

It is well known that if the three dimensions of the elastic body are altered in the same proportion, the wave-frequencies of its transverse vibrations change also in the same but inverse proportion, higher frequencies corresponding to smaller dimensions. Thus if we compare two rods of the same material, the one of length l , breadth b , and width w , and the other of length $a.l$, breadth $a.b$, and width $a.w$, the wave-frequencies of their transversal vibrations are in the ratio $1:a$, while the volumes are in the proportion $1:a^3$. Hence the wave-frequencies are inversely proportional to the cube roots of the volumes. Now, it appears that in the case of vibrating atoms a similar, although not quite so simple, relation obtains. In each group of chemically related elements, such as the alkalis for instance, the wave-frequencies of the tails, ν_∞ , can be approximately represented by an equation

$$\nu_\infty = m + \frac{n}{\sqrt[3]{v}}, \quad (19)$$

where m and n are constants and v denotes the atomic volume of the element. As an example, let us take the wave-frequencies ν_∞ of the following five elements, referring to the first components of the subsidiary series:

v		$1/v_1$	ν_∞	Computed.
Li:	11.8	0.43925	28589	28514
Na:	23.7	0.34814	24486	24660
K:	45.0	0.28115	21994	21827
Rb:	56.0	0.26138	20965	20990
Cs:	79.0	0.23306	19748	19792

The values of the last column are those computed from the equation

$$\nu_\infty = 9934 + \frac{42300}{\sqrt[3]{v}}.$$

The atomic volumes have been taken from the data given in the article "Chemistry" in the *Enc. Brit.* To expect more than a merely approximate agreement seems scarcely warranted, considering the uncertainties in the values of v here adopted. In spite of the doubtless large discrepancies between the values of the last two columns, I am inclined to think that the asserted relation between the wave-frequencies ν_∞ and the linear dimensions of the atoms expresses a real physical law. The view is supported by the following interesting fact. In the vertical column of MENDELEJEV'S system

which contains the five elements here considered we find also Hydrogen, which with regard to chemical valency is certainly related to our group of metals. Supposing, then, that Hydrogen belongs to the same group, we may, since we know the wave-frequency of the tail of its subsidiary series, compute its atomic volume. With $\nu_{\infty} = 27426$ we find from the preceding equation

$$v = \left(\frac{42300}{17492} \right)^3 = 14.1.$$

Since the atomic volume is defined as the atomic weight divided by the specific gravity of the substance in the solid state, we conclude that solid hydrogen should be 14 times lighter than water. It is interesting to see that for the specific gravity of the liquid at the lowest attainable temperature the same value was found by Professor DEWAR in his celebrated experiments on the liquefaction of gases. The close agreement may perhaps be accidental, especially since we do not know how much the specific gravity may change in the transformation of the gas from the liquid to the solid state, but nevertheless it seems that the new relation assigns to Hydrogen spectroscopically its correct position in the group of elements to which it is chemically related. The difficulty which appears in the attempt to connect, in this group, the position of the tails with the atomic *weights*, no longer comes in when atomic *volumes* are considered.

In other groups the same relation, with altered constants, is noticeable. Thus we find :

v	$1/\nu_1$	ν_{∞}	Comp.	v	$1/\nu_1$	ν_{∞}	Comp.
Mg : 13.7	0.41792	39780	39850	Zn : 9.1	0.47898	42925	42889
Ca : 25.4	0.34019	33919	33779	Cd : 12.9	0.42638	40766	40840
Sr : 34.8	0.30629	31060	31130	Hg : 14.7	0.40822	40168	40130
$\nu_{\infty} = 7203 + \frac{78112}{\sqrt[3]{v}}$				$\nu_{\infty} = 24228 + \frac{38960}{\sqrt[3]{v}}$			

On the other hand, however, the relation is not fulfilled for the elements Al, In, Tl, which Professor KAYSER considers as a group of the third vertical column of MENDELEJEV'S system. But whether the three metals are indeed chemically coordinated, and should therefore be grouped together, is still somewhat doubtful.

I am not contending, however, that the existence of the asserted relation between the wave-frequencies of the tails and the atomic volumes is conclusively proved by the preceding figures. So far as we may judge from the scanty materials at our disposal, we can only venture to say that indications in its favour seem to be present among the observations. Unfortunately it is not very probable that we shall learn more on this point in the future, as far as observations are concerned. Nevertheless the suggestion is perhaps valuable from the theoretical point of view, and for this reason a reference to it was thought advisable at this stage of the investigation. With regard to

the constant n of equation (19) some evidence may be brought forward which seems to point to the conclusion that in the various groups n is always an integral multiple of one and the same number. For instance, we have seen that in the Mg-group n had almost exactly twice the value of that in the Zn-group. If, in the various groups, we assume for m (equation 19) the values

Li-group :	$m = 10580$
Mg-group :	6536
Zn-group :	23772

the following comparison will show that by assuming $n = 4 \times 10^4$ or 8×10^4 we can approximately represent the wave-frequencies of the tails of the subsidiary series :

	ν_z	Comp. ($n = 4 \times 10^4$)		ν_z	Comp. ($n = 8 \times 10^4$)
Li :	28589	28150	Mg :	39780	39970
Na :	24486	24506	Ca :	33919	33752
K :	21994	21826	Sr :	31060	31040
Rb :	20965	21035			
Cs :	19748	19902			
				ν_∞	Comp. ($n = 4 \times 10^4$)
			Zn :	42925	42931
			Cd :	40766	40827
			Hg :	40168	40101

Applying the relation (19) to the principal series of the alkali-group, we find for the two elements of lowest atomic weight Li and Na, $n = 2 \times 10^4$, but for the three others K, Rb and Cs, $n = 8 \times 10^4$, with the corresponding values of m : 34610 and 12758.

	ν_z	Comp.		ν_z	Comp.
Li :	43498	43395	K :	35030	35250
Na :	41468	41573	Rb :	33762	33668
			Cs :	31526	31402

Again we have to confess, however, that the materials at our disposal are too limited to demonstrate the alleged property of the quantity n conclusively, and hence that it is useless to enter upon further comment. The history of the subject here discussed must warn us to state such regularities with due reserve, and not to rush to hasty conclusions, however tempting they may be.

I shall now discuss in a few words some interesting results with regard to the constant a_1 of the RYDBERG-THIELE equation. It was shown at the beginning of this investigation that we can write

$$\nu = \nu_\infty - \frac{1}{a_1} (m + \mu)^{-2} - \frac{b_1}{a_1^2} (m + \mu)^{-4} \dots$$

an equation which assumes the form of RYDBERG's formula when $b_1 = 0$. As is well

known, Professor RYDBERG had assumed that the factor $\frac{1}{a_1}$ should be a constant for all the line-series. KAYSER, however, showed that this assumption had to be abandoned because it led to quite inadmissible discrepancies in the computed wave-lengths. In his own formula the value of $\frac{1}{a_1}$ ranges between 109625 for Li and 155562 for Al, and thus "varies only within narrow limits for the various elements" (*Handbuch*, vol. ii. p. 516). At another place he remarks that "probably in the true formula, which neither he nor RYDBERG had found, this factor may indeed be a constant." Let us now see how far $\frac{1}{a_1}$ changes if the RYDBERG-THIELE formula is employed. In this comparison between the various elements we must confine our attention to the subsidiary series, because so far principal series are only known for the elements of the group of alkalis and for Helium. Now we notice at once that the values of $\frac{1}{a_1}$ are certainly not the same for different spectra, since they range between 109575 for Li and 124020 for Cs. But the variations are doubtless much smaller than in Professor KAYSER's formula. Since the *a priori* presumption may perhaps be admitted that the changes of $\frac{1}{a_1}$ may be connected with the position of the element in MENDELEJEFF's system, I have arranged the following table, which shows the constants in this order :

I.	II.	III.	VI.
1. H: 109704			
2. Li: 109575			O: 110118
3. Na: 110788	Mg: 112512	Al: 114590	S: 110367
4. K: 116430	Ca: 111363		
5. Cu: 109726	Zn: 114265		Se: 109345
6. Rb: 123572	Sr: 117292		
7. Ag: 109410	Cd: 114250	In: 117398	
8. Cs: 124020			
9. ...			
10. ...			
11. ...	Hg: 112838	Tl: 114015	

The system is that published in vol. 71 of *Nature*, p. 66. In all cases where more than one subsidiary series is known, I have taken the arithmetical mean of the constants computed from each series. One interesting fact is at once revealed by the figures of this table, viz. that the changes are greatest in the first vertical column, the difference between the largest and smallest values of $\frac{1}{a_1}$ being respectively, column I. : 14445; column II. : 5929; column III. : 2808; column VI. : 1022. But another important feature is shown if we compare the horizontal rows 1, 2, 3 . . . 11. In the odd rows 3, 5, 7 and 11 the numbers increase at first, reach a maximum, and then

decrease again. In the even rows 4 and 6, on the other hand, there is a rapid decrease from column I. to column II.

Now, by a course of reasoning upon which I shall not enter here, I have been led to investigate a phenomenon which curiously shows the same regularities, although at first sight it may appear difficult to perceive its causal connection with the changes of our constants. I refer to the effects of pressure on the displacements of the spectral lines. If we take these displacements from the results of HUMPHREY and MOHLER's well-known researches and arrange them in MENDELEJEV'S system, we obtain the following table of values, in which the displacements are given in $\frac{1}{10000}$ th of a tenth-metre, and correspond in each case to a change of pressure of 12 atmospheres:

	I.	II.	III.	IV.	V.	VI.	VII.	VIII.		
1										
2										
3	Na 25	Mg 46	Al 55	Si 43						
4	K 130	Ca 27/54		Ti 19	V 25	Cr 26	Mn 23	Fe 25	Ni 28	Co 24
5	Cu 33	Zn 57			As 35					
6	Rb 130	Sr 37/65	Y 15	Zr 28	Nb 34	Mo 40			Rh 30	Pd 33
7	Ag 39	Cd 80	In 88	Sn 55	Sb 49					
8	Cs 160	Ba 34/58	La 32	Ce 27						
9										
10							W 19	Os 19		Pt 20
11	Au 49	Hg 81	Tl 61	Pb 60	Bi 49					

Evidently these figures show the same features as the values of $\frac{1}{\alpha_1}$ discussed before.

The amplitude of the changes is again decidedly greatest in column I., and decreases rapidly, being quite insignificant in columns VII. and VIII. We notice further that in the odd horizontal rows 3, 5, 7 and 11 the displacements tend from small values towards a maximum and decrease afterwards, whereas the even rows 4, 6 and 8 begin with high figures, which diminish rapidly and asymptotically approach a constant minimum value. It is also worth mentioning that those cases where two kinds of displacements have been observed by Messrs HUMPHREY and MOHLER, *e.g.* Ca, Sr, and Ba, belong to this second class. Are we allowed, then, to conclude that a connection exists between the displacements of the lines through changes of pressure and the constants α_1 of the RYDBERG-THIELE equation? Obscure and seemingly unfathomable as these phenomena are at present, they cannot but open new vistas of thought and instigate theoretical research.

In my demonstration of the superiority of the RYDBERG-THIELE equation over that of KAYSER and RUNGE I hope that I may not have conveyed the impression that I was insensible of the undoubtedly great merits of the latter. Everyone who has studied the problem here discussed cannot but recognise how much we are indebted to Professor KAYSER and his co-workers for the enormous advance of our knowledge in this field of spectroscopic research, an advance which without his empirical formula would not have been possible. Our feeling of admiration and gratitude for this great physicist's work in a novel and difficult sphere of optics, to which he has so long and successfully devoted his high scientific abilities, will doubtless stand unabated even if his formula should not be finally accepted as the mathematical expression of the law of those marvellous spectral regularities, the knowledge of which we owe chiefly to his ingenious investigations.