The dummy tubes had thus actually lost slightly more in alkalinity than the tubes through which the air had passed. This loss is about equal to what would be caused by the absorption of the carbonic acid contained in 6 litres of pure air.

It follows from this and the other experiments just referred to that the error with the tube method may be considerable, at least in experiments of not more than two or three hours' duration.

XXXIV. *On the Structure of the Line-Spectra of the Chemical Elements. By* J. R. RYDBERG, *Ph.D., Docent at the University of Lund**.

(PRELIMINARY NOTICE.)

THE researches, the most important results of which are given in the following pages, will be published with full details in the *Svenska Vetensk.-Akad. Handlingar Stockholm.* They have extended hitherto only to the elements which belong to the groups I., II., III. of the periodical system ; there is, however, no reason to doubt but that the laws I have found can be applied in the same way to all elements.

In my calculations I have made use of the *wave-numbers* (n), instead of the wave-lengths (λ) ; $n = 10^8 . \lambda^{-1}$, if λ be expressed in Ångström's units. As will be seen, these numbers will determine the number of waves on 1 centim. in air (760 millim., 16° C. according to Ångström), and are proportional, within the limits of the errors of observation, to the numbers of vibrations.

1. *The " long " lines of the spectra form doublets or triplets, in which the difference (ν) of wave-numbers of their corresponding components is a constant for each element.*

This law, found independently by the author, has already been announced by Mr. Hartley for Mg, Zn, Cd. The values of the constant differences (ν) vary from $\nu = 3 \cdot 1$ in the spectrum of Be to $\nu = 7784 \cdot 2$ in the spectrum of Tl. In each group of elements the value of ν increases in a somewhat quicker proportion than the square of the atomic weight. For instance :—

* Communicated by the Author.

Element ...	B.	Al.	Ga.	In.	Tl.
P	10·9	27·04	69·9	113·4	203·7
ν	10·5	109·6	823·6	2212·4	7784·2
$\dfrac{100\nu}{P^2}$	8·84	14·99	16·86	17·20	18·76

In accordance with analogy, the spectral lines of Li (the one element, besides H, in which only single lines are observed) ought to be double with $\nu = 0.8$, corresponding, for instance, in the red line ($\lambda = 6705.2$) to a difference in λ of 0·36 tenth-metre. The most refrangible of the components should also be the strongest.

The elements of the groups I. and III. (atomicity odd) have only doublets; triplets are found in the elements of group II. (atomicity even). As examples may be cited the doublets of Tl and the triplets of Hg.

Thallium.

λ_1 ...	5349·5	3528·3	3229·0	2921·3	2825·4	2710·4	2669·1	2609·4	2552·0	2517·0
ν ...	7792·6	7796·6	7794·9	7785·5	7766·1	7773·9	7783·1	7781·2	7794·2	7780·7
λ_2 ...	3775·6	2767·1	2579·7	2380·0	2317·0	2238·7	2210·0	2169·0	2128·6	2104·8

Mercury.

λ_1	5460·5	3662·9	3341·2	3021·0	2925·2	2798·5
ν_1	4633·0	4644·0	4638·0	4602·9	4644·7	4626·6
λ_2	4358·0	3130·4	2892·9	2652·2	2575·3	2477·7
ν_2	1763·4	1766·1	1776·4	1761·9	1759·0	
λ_3	4047·0	2966·4	2751·5	2533·8	2463·7	

With the triplets the ratio of the two constant differences $\dfrac{\nu_1}{\nu_2}$ increases from 2·01 in Mg to 2·63 in Hg. Also with these elements (of group II.) there are doublets, which follow the same rule as the others; the value of the difference ν_0 in these doublets is about 2·2 times as great as the first difference ν_1 of the triplets in the same element. For example, we have:—

	Ca.	Zn.	Cd.
ν_0	223·2	876·5	2483·8
ν_1	103·2	388·4	1172·5
$\dfrac{\nu_0}{\nu_1}$	2·16	2·23	2·12

These doublets contain the strongest lines of the elements of group II.

2. *The corresponding components of the doublets form series, of which the terms are functions of the consecutive integers. Each series is expressed approximately by an equation of the form*

$$n = n_0 - \frac{N_0}{(m+\mu)^2} ; \qquad \cdots \cdots \quad (1)$$

where n is the wave-number, m any positive integer (the number of the term), $N_0 = 109721 \cdot 6$, a constant common to all series and to all elements, n_0 and μ constants peculiar to the series. It will be seen that n_0 defines the limit which the wave-number n approaches to when m becomes infinite.

Messrs. Liveing and Dewar were the first to remark the existence of the series, as well as their different appearances. They are of three kinds : *diffuse, sharp,* and *principal* series. The first two are formed by the above-mentioned doublets or triplets ; in the elements of the groups I. and III. there are consequently four different series of these two kinds, in the elements of group II. there are six. I have named them *first, second,* and *third* diffuse or sharp series. The lines of the first series of each kind are the strongest and the least refrangible.

Hitherto I have found the principal series only in group I. They are double, but the doublets are not of the same kind as those described in section 1 ; the components approach each other when m increases (see section 3). I name the stronger of the two series, which is also the most refrangible, *first principal series.* The principal series contain the strongest lines of the spectrum (in group I.), then come the diffuse series (the individual lines of which are in reality double ; *cfr.* section 4), the sharp series are the weakest. In the individual groups the intensity decreases as the order of the series increases, in the same way as the lines grow weaker in the individual series with increasing m.

As an example of the series and their calculation, *the principal series of Li* is as follows:—

$$\text{Formula}: \quad n = 43487 \cdot 7 - \frac{109721 \cdot 6}{(m + 0 \cdot 9596)^2}.$$

m ...	1.	2.	3.	4.	5.	6.	7.	8.	9.
λ obs.	6705·2	3232·0	2741·0	2561·5	2475·0	2425·5	2394·5	2373·5	2359·0
λ calc.	6704·8	3229·8	2740·5	2562·3	2475·3	2425·9	2394·9	2374·1	2359·5
Diff.	−0·4	−2·2	−0·5	+0·8	+0·3	+0·4	+0·4	+0·6	+0·5

3. The different series of the elements are related to each other in a way which proves that they all belong to one system of vibrations. To show these relations, I will cite as an example the formulæ of the diffuse and sharp lines of Na :—

Diffuse Group.

First series .... $n = 24481 \cdot 8 - \dfrac{109721 \cdot 6}{(m + 0 \cdot 9887)^2}$.

Second series ...... $n = 24496 \cdot 4 - \dfrac{109721 \cdot 6}{(m + 0 \cdot 9887)^2}$.

Sharp Group.

$n = 24485 \cdot 9 - \dfrac{109721 \cdot 6}{(m + 0 \cdot 6445)^2}$.

$n = 24500 \cdot 5 - \dfrac{109721 \cdot 6}{(m + 0 \cdot 6445)^2}$.

The series of the same group (diffuse or sharp) have the same value of μ; the difference of their values of n_0 is equal to ν or (ν_1 and ν_2). This follows from the fundamental property of the doublets. With Na we have $\nu = 14 \cdot 6$.

The series of the same order (first, second, third) have the same value of n_0 in the different groups; they are distinguished by the values of μ. The difference, for instance, of the numbers 24481·8 and 24485·9, which are perfectly independent of each other, amounts only to 0·7 tenth-metre. We find in all the revised spectra the same accordance when we calculate the values of n_0, using only the last terms of the series. For example, if we denote the values obtained from the diffuse series by n_1 and those from the sharp series by n_2 :—

Element ...	Li.	Mg.	Cd.	Tl.
n_1	28598·5	39777·9	40775·9	41485·9
n_2	28601·1	39779·9	40789·1	41486·5

Between the principal and the sharp series there is also a very close relation. For if we write the equation (1) in the more symmetrical form

$$\pm \frac{n}{N_0} = \frac{1}{(m_1 + \mu_1)^2} - \frac{1}{(m_2 + \mu_2)^2}, \quad \cdot \quad \cdot \quad \cdot \quad (2)$$

it is found that this equation, without varying the constants μ_1 and μ_2, will represent a principal series or a sharp series, according as we assume the one or the other of the integers m_1 and m_2 to be variable ; to the number which is left unchanged we must assign the value 1.

To calculate with great approximation the spectrum of one of the alkaline metals, we use only four constants (with Li but three), the common constant N_0 not included.

By the proposal of a *system of notation* for series and lines, I have tried to show a way by which we can indicate shortly the connexion of the different parts of a spectrum with the whole system of vibrations, and which at the same time allows the correspondence of the lines of different elements clearly to appear. A few examples will suffice to show the arrangement and the use of this system. K $[D_1, 4]$ denotes the fourth line of the first diffuse series of the spectrum of potassium ($\lambda = 5801$) ; Mg $[S_2]$ the (whole) second sharp series of Mg ($\lambda = 5172 \cdot 0, 3331 \cdot 8, 2938 \cdot 5, 2778 \cdot 7, 2695, 2646$); Rb $[P_{12}, 2]$ the second doublet of the principal group of Rb ($\lambda = 4202$ and 4216); the single lines are denoted by Rb $[P_1, 2]$ and Rb $[P_2, 2]$ respectively.

4. *The wave-lengths (and the wave-numbers) of corresponding lines, as well as the values of the constants ν, n_0, μ of corresponding series of different elements, are periodical functions of the atomic weight.*

As an example, the wave-lengths of the second term ($m = 2$) of the diffuse series may be taken together with the values of ν (with the triplets ν_1 and ν_2), which are given in smaller figures in their respective places between the wave-lengths. These values of ν are means from the differences of the wave-numbers of all doublets which have been employed in the calculation. The components of the doublets are themselves double; the less refrangible of the secondary components is the weaker, but corresponds to the constant difference, and is consequently to be reckoned as the true component of the doublet.

Group of elements.		Li.	Na.	K.	Cu.	Ag.	Au.
I.	λ_1	{ 6102	8199	 12330	5217·1	{ 5470·0 { 5460·0	{ 5862·0 { 5836·0
	ν	(0·8 calc.)	14·6	56·4	242·2	917·2	3819·5
	λ_2	......	8187	......	5152·6	5208·7	4792·0
		Be.	Mg.	Ca.	Zn.	Cd.	Hg.
II.	λ_1	3130·3	3837·9	{ 4455·2 { 4454·0	3344·4	{ 3611·8 { 3609·4	{ 3662·9 { 3654·4
	ν_1	3·1	41·4	103·2	388·4	1160·2	4637·3
	λ_2	3130·0	3832·1	{ 4435·3 { 4434·5	3301·7	{ 3466·7 { 3465·2	{ 3130·4 { 3124·5
	ν_2	......	20 6	51·4	187·4	538·4	1766·0
	λ_3	......	3829·2	4425·0	3281·7	3402·7	2966·4
		B.	Al.			In.	Tl.
III.	λ_1	2497·0	3091·9	......	......	{ 3257·8 { 3255·5	{ 3528·3 { 3517·8
	ν	10·5	109·6	.....	......	2212·4	7784·2
	λ_2	2496·2	3081·2	......	......	3038·7	2767·1

The lines of Li and K are, in all probability, double like the others, but their components have not yet been separated.

The periodical variation of the constants allows of calculating by interpolation the spectrum of an element when the spectra of the adjacent elements in the periodical system are known. To show how far such an interpolation can go, I will cite the wave-lengths of the first terms of the diffuse and sharp series of Ga. They are calculated without making use in any way of the (two) measured lines of this element, or even having them present in the calculation.

The interpolated constants are (*cfr.* section 3) :—

$$n_0. \qquad \nu. \qquad \qquad \mu.$$

First series .... $47547·1$ ⎱
$\qquad\qquad\qquad\qquad$ $831·6$
Second series ...... $48378·7$ ⎰

Diffuse group ...... $0·8363$

Sharp group......... $0·1568$

and the thereby calculated wave-lengths :—

	Diffuse group.			Sharp group.		
m	1.	2.	3.	2.	3.	4.
First series ...	6663·4	2949·2	2494·3	4173·7	2737·0	2427·4
Second series...	6313·5	2878·6	2443·6	4033·7	2676·1	2379·3

The sharp doublet ($m=2$) is nearly coincident with the two lines which hitherto have been measured. The wave-lengths of these lines are, viz :—

After Lecoq de Boisbaudran.	After Deville and Mermet.
$\left.\begin{array}{c}4170\\4031\end{array}\right\}\ \nu=826\text{·}9$	$\left.\begin{array}{c}4171\\4033\end{array}\right\}\ \nu=820\text{·}3$

The accordance is even better than could well be expected.

Finally, I will remark that the hypotheses of Mr. Lockyer on dissociation of the elements are quite incompatible with the results of my researches. The observations of Lockyer within the spectra of Na and K prove only that, with luminous atoms as with sounding bodies, the relative intensity of the partial tones may vary under different circumstances. For the lines in question belong, without doubt, to the same system of vibrations.

Lund, February 1890.

XXXV. *The Change of the Order of Absolute Viscosity encountered on passing from Fluid to Solid.* By CARL BARUS.

1. TO my knowledge nobody has thus far defined the difference between the solid state and the fluid states quantitatively. In the case of liquids and gases viscosity can be absolutely expressed with facility, and the data have therefore to be stated with considerable rigour. This is not true for solids, where the results are relative throughout.

The present paper submits two methods for the coordination of the viscous behaviour of solids and of liquids. In describing the differential method applied by Dr. Strouhal and myself[†], we incidentally pointed out the way in which the relative viscosity of two solids may be stated in terms of the respective sectional areas, by which the motion at the junction of the two counter-twisted wires or rods is annulled. Suppose that one of the wires is a solid, whereas the other is a very viscous liquid. Then if the viscosity of the latter can just be measured by transpiration-methods (§§ 4, 5), it follows that the viscosity of the true solid with which it was counter-twisted may also be absolutely expressed. This indicates the first method of the present paper (§§ 8, 9).

* Communicated by the Author.
† Barus and Strouhal, American Journal, xxxiii. p. 29 (1887).