ART. IV.—*On the Distribution of the Dark Lines in the Spectra of the Elements*; by Prof. GUSTAVUS HINRICHS, Iowa State University.

As soon as I heard of the great discovery of Kirchhoff and Bunsen, I felt sure that the dark lines of the elements would prove to be distributed according to simple laws, and that these laws might lead us to a knowledge of *the relative dimensions of the atoms*. But it was only quite recently that I was enabled to study the distribution of these lines in its detail, Prof. Silliman Jr. having kindly sent me Kirchhoff's two memoirs. Yet I limited my investigation to the group of the alkaline earths and iron; for whatsoever is true for some elements will also be found applicable to the remainder of them; and besides Kirchhoff's measurements are not at all to be considered as final, neither does he give all lines that may be observed: so that the material at hand can justify only a *preliminary investigation*, to be completed and modified by more complete and more accurate observations.

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As it is well known that some distinguished American experimenters are engaged in a more accurate and complete survey of the spectra, I thought it proper to give the results of this preliminary research in order that the remarkable laws here found as the essence of Kirchhoff's determinations might as soon as possible be further developed.

It might seem that such an investigation could not lead to definite results, since Kirchhoff's scale is entirely arbitrary and even changing. But within a small range equal differences on this scale must correspond to equal differences in wave length, for whatever the curve may be (we have found it to coincide with a parabola), representing the wave-length as a function of Kirchhoff's millimetre-scale, within such narrow limits the curve will coincide with its tangent. We must therefore first see whether the different *groups of lines* exhibit any order.

Commencing with the *Calcium-spectrum*, we find a group of lines near Fraunhofer's G. Representing the intensity by I, the scale-division by K, the successive differences by D, we find from Kirchhoff's table—

Group I, $d_1 = 5.0$.

I.	K.	D.	i.	C.	E.
5c	2869.7	5.0	1	2869.7	.0
4b	64.7	10.0	2	64.7	.0
4	54.7	20.5	4	54.7	.0
5c	34.2			34.7	+5

It is plain that the values of D are as 1 : 2 : 4; considering these ratios as intervals, *i*, and calculating from them and the difference the values C, which would correspond to a perfectly regular distribution of the lines, we obtain the error of this theoretical determination $E = C - K$, as given in the last column. We see, the error is almost nothing—the last one might easily be conceived as the result of the increased range. Hence we find that this group is very regular, having a principal difference of 5.0, or a simple multiple (here successive duplication) thereof.

The *second group*, stretching from 2653.2 mm. to 2605.8 mm., has a range of 47.4 mm., which appears to be rather large; yet we find (comparing lines of high and similar intensity, those of lower intensity not being uniformly given):

Group II, $d_2 = 2.026$.

I.	K.	D.	i.	C.	E.
{ 5b	2653.2			53.2	0.00
{ 1d	(52.9)				
{ 5c	38.8	14.4	7	39.02	+22
{ 4c	(38.5)				
3c	(7.1)				
5c	6.6	32.2	16	6.60	—00
3b	(5.8)				

The intervals are not in any simple ratio, but closely approach to 1 : 2, yet the great range of this group does not authorize us to give great weight to it.

Group III, $d_3 = .75$. A very bright group of small range.

I.	K.	D.	i.	C.	E.
4b	1533.1	.6	1	33.2	+ .10
4b	32.5	2.3	3	32.45	— .05
4c	30.2	1.5	2	30.20	.00
5c	28.7	6.0	8	28.70	.00
6c	22.7			22.70	.00

These errors are certainly within the errors of observation. The intervals seem to be rather irregular, but combining the first two we have 4 : 2 : 8, or 2 : 1 : 4. The signification of such combinations will become apparent in the sequel.

Group IV, $d_4 = 1.3$.

I.	K.	D.	i.	C.	E.
3d	1235.0	5.4	4	34.8	— .2
4c	29.6	1.3	1	29.6	.0
2d	28.3	3.6	3	28.3	.0
5d	24.7	3.1	2	24.4	— .3
5d	21.6	2.4	2	21.8	+ .2
3c	19.2	1.4	1	19.2	0.0
5d	17.8			17.9	+ .1

Group V, $d_5 = 3.5$.

I.	K.	D.	i.	C.	E.
2e	894.9	10.0	3	895.4	+ .5
4b	84.9	21.0	6	84.9	.0
5b	63.9	3.7	1	63.9	.0
3d	60.2			60.4	+ .2

only having an error in the extremes.

Group VI, $d_6 = 2.3$.

I.	K.	D.	i.	C.	E.
5b	740.9	4.0	2	40.8	— .1
3b	36.9	5.2	2	36.2	— .7
5b	31.7	2.7	1	31.6	— .1
2b	29.0	8.9	4	29.3	+ .3
2c	20.1	2.3	1	20.1	.0
2b	17.8			17.8	.0

The error of .7 is considerable in regard to d_6 and in general; yet it will disappear if we combine the first two intervals, thereby at the same time obtaining the simple series 4 : 1 : 4 : 1, or showing the whole group to consist of two equal parts of 5, each again composed of 4 : 1. Besides, it must be observed that the line 36.9 is faint as compared to the inclosing ones, marking plainly a subdivision as intimated.

These numbers seem to justify our first law :

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I. *The mutual distances of the different lines in each separate group are multiples of the smallest distance in such group.*

To proceed further, we must remember that Kirchhoff himself acknowledges that he did not map all the lines he saw; besides, we know that many lines have been discovered which he did not see. Now the intensity of a line is certainly a less important element than its place; hence it may be that some lines are mapped while corresponding ones are not. Thereby we are permitted to group several lines into one group which we will call a *physical combination*, since it consists entirely of actually observed lines. It would, on account of the above, likewise be proper to admit hypothetical lines, thus dividing a given interval into a *virtual combination*; but since such divisions are given by the numbers representing the interval, and since we desire to keep this part of our article entirely free from any hypothesis, it being our purpose to show just what the given facts mean—we will not make any further use of such virtual combinations; what is here said will be sufficient to make the experimenter look to those places of the spectrum which are pointed out by such combinations.

The six groups of the calcium spectrum show the following remarkable physical combinations:

Group I, interval: observed 1 : 2 : 4.

Group II, range too great, interval approaching the ratio of 1 to 2.

Group III, observed 1 : 3 : 2 : 8

physical $\overbrace{4 : 2 : 8}$, or $\overbrace{2 : 1 : 4}$

Group IV, observed 4 : 1 : 3 : 2 : 2 : 1

physical 4 : $\overbrace{4 : 2 : 2 : 1}$

or 4 : 4 : $\overbrace{4 : 1}$

Group V, observed 3 : 6 : 1

Group VI, observed 2 : 2 : 1 : 4 : 1

physical $\overbrace{4 : 1 : 4 : 1}$

or $\overbrace{5} : \overbrace{5}$

These numbers show :

II. *The intervals in the different groups may be expressed in very simple numbers, as 1, 2, 3.*

Thus there is a very great harmony between the intervals of the same group. If this harmony is to be admitted as a physical fact, it must extend throughout the whole spectrum of an element. And if our notion of a physical group, as containing corresponding lines, is correct, these physical groups must have corresponding intervals throughout. We find from the preceding tables:

	Physical interval.
Group I, $d_1=5\cdot0$	$\Delta_1=2d_1=10\cdot0$
[" II, $d_2=2\cdot026$	$\Delta_2=5d_2=10\cdot13$
" III, $d_3=.75$	$\Delta_3=14d_3=10\cdot5$
" IV, $d_4=1\cdot3$	$\Delta_4=8d_4=10\cdot4$
" V, $d_5=3\cdot5$	$\Delta_5=3d_5=10\cdot5$
" VI, $d_6=2\cdot3$	$\Delta_6=4d_6=9\cdot2$
	$5d_6=11\cdot2$

Group II is enclosed in brackets, because its wide range made us exclude it in the preceding; besides $5d_2$ is but a virtual interval, not marked by actually known lines. Δ_6 is somewhat indeterminable; yet it probably is $4d_6$ on account of the differences between Kirchhoff's scale and the natural scale of wave-lengths being for this group considerable. The whole of the brilliant group III has been considered as Δ_3 , it forming decidedly a natural group. The great approximation of the values of Δ , distributed over almost the whole range of the spectrum, seems to justify the following conclusion:

III. *The difference in wave-length between the corresponding lines in a group is the same throughout the whole spectrum.*

It will be borne in mind that we did not select the groups to lead to such a law, but that we here—as actually was the case in finding this law—simply took the physical groups before given.

Hitherto we have never compared greater intervals than $\Delta=10$, taken in different parts of the spectrum; for such the corresponding wave-lengths will prove very nearly equal throughout. But now we must farther compare not the range of a group but the interval separating the different groups. Evidently the single lines interspersed between the groups will have the same physical signification; they may prove to be the only yet known members of less intense groups.

Comparing the values of Kirchhoff's scale with the well known wave-lengths of Fraunhofer's principal lines, we found by a graphical interpolation the following reduction to wave-length for the various single lines or groups:

I.	K.	Wave length	Differences
		$G=0^{mm}00042\cdot91+$	if $\delta=8$.
Group I,	$287\frac{5}{8}$	$+ 0\cdot0$	
" II,	$265\frac{3}{8}$	$1\cdot5$ to $1\cdot9$	$= 2\delta - 1$ or $+ 3$
6c,	2058·0	5·7	$7\delta + 1$
2c,	1832·8	7·4	$9\delta + 2$
5b,	1627·2	8·9	$11\delta + 1$
" III,	$152\frac{3}{4}$	9·6 to 9·8	12δ
2b,	1443·5	10·5	$13\delta + 1$
" IV,	$127\frac{1}{2}$	12·8	16δ
3c,	1029·3	15·4	$19\delta + 2$
" V,	$82\frac{5}{8}$	19·7	$25\delta - 3$
" VI,	$74\frac{1}{4}$	22·3	$28\delta - 1$
2b,	641	23·0	$29\delta - 2$

Greater degree of accuracy can not be attained before we have direct measurements of these wave-lengths like those recently made by Eisenlohr. The existing facts give these differences as multiples of $\delta = 8 = 0^{\text{mm}} \cdot 000008$ between the different groups of lines,

The intervals appear not very regular, but smallest (equal to δ) near the brilliant group III. Extending our view of physical combinations (i. e., such as are marked by actually known lines) to the whole of the spectrum, we obtain the following intervals:

Observed, 2 : 5 : 2 : 2 : 1 : 1 : 3 : 3 : 6 : 3 : 1

Physical, 2 : 5 : $\overbrace{6}^{\quad}$: $\overbrace{6}^{\quad}$: 6 : 3 : 1

or $\overbrace{7}^{\quad}$: 6 : 6 : 6 : 4

both of which are almost as simple as possible. The latter would be formed of equal intervals, 6, if the last interval extended beyond 641 mm. K, and if some line should be discovered within the last observed interval, i. e., about midway between 2650 and 2840 mm. K. Hence the existing observations make it very probable that

IV. *The principal corresponding lines or groups of lines are equidistant in regard to their wave-lengths.*

It will be perceived that these successive laws may be considered as generalizations of the same principle. Hence it is of the utmost importance to see how far other substances give evidence of the same laws. We will first consider the other alkaline earths.

The spectrum of *strontium*, as given by Kirchhoff, is too deficient yet to be of any consequence.

The *barium* spectrum is more complete, but we have too few lines to discern the physical groups; therefore it seems best to rely on the more intense lines as corresponding ones.¹ We obtain as before:

I.	K.	$G = 0^{\text{mm}} \cdot 00042 \cdot 91 +$	Differences.
{ 1b	2502.4		
{ 4c	.2		$\delta = 1.1$
6b	2461.2	2.8	$\underline{\underline{3.4 = 3\delta + .1}}$
2c	2031.1		
6c	1989.5	6.2	$4.8 = 4\delta + .4$
1b	1371.4	11.0	
1c	1287.5		$1.1 = \delta$
3b	1274.2	12.1	$2.2 = 2\delta$
2a	1083.0	14.3	$1.1 = \delta$
2a	1031.8	15.4	
1b	890.2		$3.1 = 3\delta - .2$
4b	874.3	18.5	
3a	719.6	19.8	$1.3 = \delta + .2$
2	718.7		

¹ Except where single lines occur in great distances, for they probably represent the more intense ones of those parts.

Giving the intervals

Observed, 3 : 4 : 1 : 2 : 1 : 3 : 1

Physical, 3 : 4 : 4 : 4

These numbers thus confirm the conclusions drawn from the calcium spectrum. At the same time there appears yet one most remarkable new relation if we compare the interval 4δ of barium, which interval seems to be a physical one, with the corresponding interval 6δ of calcium. For we have

Calcium, $\delta = .8$ hence $6\delta = 4.8$

Barium, $\delta = 1.1$ " $4\delta = 4.4$

or only a difference of $0^{\text{mm}}.000004$ in wave-length between numbers as large as $0^{\text{mm}}.00005$. Is this physical interval for calcium actually the same as that for barium? Only more accurate observations can decide it; but if it proves equal, very great consequences will flow out of it.

The *magnesium* spectrum is represented by Kirchhoff as but one brilliant group. We have:

I.	K.	D.	i.	C.	E.
6e	1655.6	6.8	1	55.8	+ .2
6f	48.8	14.1	2	48.8	0.0
{ 4c	34.7			34.8	+ .1
{ 6g	34.1				

showing $d=7.0$ and conform to the first and second laws (I. and II).

Thus the four laws, first found for the calcium spectrum, are true for all the members of the group of alkaline earths, as far as their spectra are known. From this we conclude that they are essentially correct for all elements. How far this generalization is warranted we will now test by one of the most remarkable spectra: the brilliant and rich spectrum of *iron*, especially the three great groups of lines in this spectrum, groups almost without parallel both in regard to range, intensity, and closeness of the lines. Using the same signs as before, we have:

IRON, Group I, $d_1 = .8$, $\Delta_1 = 7d_1 = 5.6$.

I.	K.	D.	i.	C.	E.
4b	1200.6	6.7	8	1200.6	0.0
5g	7.3	10.5	13	7.4	+ .1
5d	17.8	13.5	17	17.8	.0
5d	31.3	8.6	11	31.4	+ .1
4a	39.9	2.7	3	40.2	+ .3
6c	42.6	3.0	4	42.6	.0
4d	45.6			45.8	+ .2

Intervals, observed, 8 : 13 : 17 : 11 : 3 : 4

physical, 21 : 28 : 7
or, $3\Delta_1$: $4\Delta_1$: Δ_1

thus having the simple ratio 3 : 4 : 1, and giving the physical difference $\Delta_1 = 7d_1 = 5.6$.

Group II, $d_2 = .8$, $\Delta_2 = 7d_2 = 5.6$

I.	K.	D.	i.	C.	E.
4d	1337.0	6.5	8	37.4	+ .4
6c	43.5	7.6	9	43.8	+ .3
5d	51.1	1.6	2	51.0	- .1
5b	52.7	10.2	12	52.6	- .1
5b	62.9	4.1	5	63.0	+ .1
6d	67.0	5.6	7	67.0	0.0
5b	72.6	7.9	10	72.6	0.0
4c	80.5	4.2	5	80.6	+ .1
4c	84.7	4.7	6	84.6	- .1
6c	89.4	1.5	2	89.4	0.0
5d	90.9	6.6	8	91.0	+ .1
5c	97.5	4.1	5	97.4	- .1
4c	1401.6	8.9	9	1401.4	- .2
4c	10.5	11.0	14	10.2	- .3
6c	21.5	1.5	2	21.4	- .1
5b	23.0	2.4	3	23.0	0.0
5b	25.4	2.8	3	25.4	0.0
5b	28.2			27.8	- .4

As starting point for C we made $E=0$ for the principal lines in the middle of the group, i. e., 67, 6d; and 89, 6c. Around these lines E are very small, but one extremity ΣE is positive, on the other negative: thus plainly indicating that the greater values of E are due to the great range—almost 100 mm. K—of the group, a range so great that the wave-lengths can not throughout fully correspond to the values K on Kirchhoff's scale.

As to the intervals, they again seem at first sight to be very capricious; yet we find

i, observed, 8 : 9 : 2 : 12 : 5 : 7 : 10 : 5 : 6 : 2 : 8 : 5 : 9 : 14 : 2 : 3 : 3

physical, 17 : 14 : 22 : 21 : 14 : 14 : 8
or, $2\Delta_2 + 3d_2 : 2\Delta_2 : 3\Delta_2 + d_2 : 3\Delta_2 : 2\Delta_2 : 2\Delta_2 : \Delta_2 + d_2$

the extremities of which series may be adjusted by extending the observation, thus giving

$3d_2 + 2\Delta_2 : 2\Delta_2 : 3\Delta_2 + d_2 + 3\Delta_2 : 2\Delta_2 : 2\Delta_2 : \Delta_2 + d_2,$

a symmetrical series of $7\Delta_2$, on each side of the median d_2 , and on the left $3d_2$, on the right $\Delta_2 + d_2$ or $8d_2$; yet it may be that further observations will reduce the great interval $22d_2$ to $21d_2$, and thereby simplify the series. We must accept the observations at hand, and these show that $\Delta_2 = 7d_2$ is the physical difference of this group, and that these divisions of higher order are again simple, symmetric in regard to the middle of the whole group. It will be noticed that not only $\Delta_2 = \Delta_1$, as ought to be, but that even $d_2 = d_1$.

Group III, $d_3=9$; $\Delta_3=3d_3=2\cdot7$.

I.	K.	D.	i.	C.	E.
5c	2001·6	3·6	4	2001·6	0·0
6d	5·2	2·0	2	5·2	·0
6c	7·2	33·9	38	7·0	— ·2
6c	41·3	·9	1	41·2	— ·1
6b	42·2	15·8	18	42·1	— ·1
6c	58·0	8·2	9	58·3	+ ·3
5c	66·2	·9	1	66·4	+ ·2
5c	67·1	14·9	17	67·3	+ ·2
6a	82·0			82·6	+ ·6

The great value of the last E undoubtedly is caused by the great range of the last interval at the end of a great group; all the other values of E are very small.

The intervals are

Observed,	4 : 2 : 38 : 1 : 18 : 9 : 1 : 17
Physical,	$\underbrace{6} : \underbrace{39} : \underbrace{18} : \underbrace{9} : \underbrace{18}$
or,	$2\Delta_3 : 13\Delta_3 : 6\Delta_3 : 3\Delta_3 : 6\Delta_3$

and these intervals of second order,

$$\underbrace{2 : 13} : \underbrace{6 : 3} : 6$$

$$\underbrace{15} : \underbrace{15}$$

give further

thus again a symmetric division—here into equal parts—of this great group.

The value of Δ_3 differs considerably from $\Delta_1=\Delta_2$; but it is obvious that $2\Delta_3=5\cdot4$ is almost the same as $\Delta_1=\Delta_2=5\cdot6$.

These most magnificent groups of the elementary spectra thus fully confirm the four laws deduced from the calcium spectrum and extended to the alkaline earths. Hence we may conclude that those laws, in substance, will be found applicable to all elementary spectra. But until much more rich and accurate measurements, combined with direct determinations of wave-length, have been made, a further prosecution of this investigation will be useless; we therefore content ourselves with this preliminary research, hoping that future investigations based upon richer material will extend these laws, and by dividing the larger intervals, prove that these remarkable lines are not distributed at random but as regular as the stripes produced by diffraction.

As far as the observations are now at hand, the above four laws seem to point to the following one, including them all:

The dark lines of any element are regularly distributed over all the spectrum, in equidistant groups consisting of equidistant lines; but the intensity of these lines regularly increases and diminishes, so as to obliterate a number of lines and even of groups, thus producing gaps in the regular series, gaps which only by high optical powers—intense line of light and great condensing lens—can be completed.

Such observations therefore are most ardently desired, and it seems urgent to construct telescopes for this particular purpose.

If we, in the preceding, have succeeded in making the regularity of the apparently highly irregular lines probable—for they certainly show definite and simple laws in their distribution—it may naturally be asked: what *causes* this distribution, and what will probably be the reward of continued researches in this direction?

The lines can only have one of the following two sources. They are either produced by the dimensions of the solid particles or by the intervals between them, i. e., their distances. The latter is impossible, for these lines remain absolutely the same under such different circumstances as cannot but to some extent change the mutual distance of the particles. *Hence the lines must be produced by the bulk of the particles or atoms themselves, and an exact knowledge of these laws and distances must lead us to a knowledge of the relative dimensions of the atoms, both as to length, breadth, and thickness.* Thus optics will give us the form and size, as chemistry has given us the weight of the atoms. The remarkable result attained by comparing the distance between the calcium groups (4·8) and the barium groups (4·4) seems to show that *one dimension* of the atoms of these two elements is nearly—or if the above values should be found to be exactly equal—perfectly equal. How great the interest of such determinations is in regard to the constitution of the elementary bodies needs not to be accentuated. It may yet lead to an experimental demonstration of the existence of a primitive substance, the element of the elements.

How the dimensions of the atoms produce these lines is another question, and it is very difficult even merely to suggest any probable connecting link between the dimension of the atoms and the luminous wave. But this can not be any serious obstacle to the practical application to *the analysis of the elements*: for so the alkalies were decomposed by electricity although the causal connection manifested therein is but imperfectly known even at the present day.

But, however this may be, we hope those physicists who are favored by the necessary delicate apparatus will find in this unpretending preliminary investigation sufficient inducement to test—and as we think probable—to confirm and complete the result here deduced from the existing observations, that: *the dark lines of the spectra of elementary bodies are regularly distributed.*

Iowa City, March, 1864.