

LVI.—*On Homologous Spectra.*

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IN June, 1881, I presented to the Chemical Society a "Note on certain Photographs of the Ultra-violet Spectra of Elementary Bodies" (*Chem. Soc. J.*, **41**, 84). Photographs were published with the note, and attention was particularly directed to the extraordinary similarity between the groupings of lines in the spectra of magnesium, zinc, and cadmium, copper, silver, iron, cobalt, and nickel. It was rendered evident that the spectra of elements of the same homologous series present either homologous* spectra or homologous groups of lines in their spectra; but it was remarked, "Whether there are numerical relations between the wave-lengths of different groups of lines, it will be hopeless to determine until the spectra have been reproduced on an enlarged scale, and the wave-lengths for the principal lines of the different elements calculated."

Similarities in the visible spectra of zinc and cadmium, of calcium, strontium, and barium, and in those of the alkali metals were observed by N. Mitscherlich (*Pogg. Ann.*, **121**, 459) and by Lecoq de Boisbaudran (*Spectres Lumineux*). From the observations of the spectra of 31 elements, Ciamician was led to the conclusion that in the spectra of chemically related elements there is a correspondence between single lines or groups of lines. Each natural group of elements has its own peculiar spectrum, and certain lines and groups of lines recur with decrease or increase of wave-length for differences in the spectra of different elements of any one group. Almost every element has a number of feeble lines which bear the same relation to

* Homologous, *i.e.*, possessing an affinity depending on structure or constitution.

the chief line or lines which the over-tones in music bear to the fundamental note.

An increase of wave-length of homologous lines of similar elements corresponds with a greater intensity of chemical kinetic energy (*Intensität der Chemischen lebendigen Kraft*). (*Über die Spectren der Chemischen Elemente und ihrer Verbindungen. Sitzungsberichte der Kaiserlichen Akademie, Wien*, **76**, 499). These observations refer only to the visible rays, or about one octave of the spectrum, but photographs of the ultra-violet region may be easily extended to two octaves above the least refrangible red line, and thus similarities in spectra not hitherto discernible have been made apparent. The conclusions of Ciamician just quoted are completely confirmed by photographs of the ultra-violet region. Dr. G. Johnston Stoney has shown (*Proc. Royal Irish Academy*, **1**, Series II, p. 107) that the spectra of gases are to be referred to faradic motions within the individual molecules, and not to the irregular journeys or encounters of the molecules with each other. The three hydrogen lines, *h*, *F*, and *C*, are shown to be the 32nd, the 27th, and the 20th harmonics of a fundamental vibration whose wave-length is 0.013127714 of a millimetre. There is evidently a harmonic relation between the lines in the spectra of magnesium, zinc, cadmium, aluminium, and in calcium, strontium, and barium, when two octaves of the spectra are examined. The fundamental vibrations appear to be in the infra-red region.

It was my original intention to bring forward an extended series of observations on the constitution of the spectra of metallic and non-metallic elements, but from a note in the Journal of this Society, *Abstr.*, **44**, 262, it seems possible that Professors Liveing and Dewar may be engaged in prosecuting a similar line of research, and I beg therefore to be allowed to lay before the Chemical Society such details concerning the published photographs as are now in hand.

Mr. W. E. Adeney has been engaged in collaboration with me in accurate determinations of the wave-lengths of lines in 20 spectra, and a few of our numbers have been employed in the following calculations, but a complete series of measurements of 16 of these spectra have been submitted to the Royal Society. In order that harmonic relations between lines and groups of lines may be conveniently studied, it is necessary to map spectra according to their *inverse wave-lengths* or *oscillation frequencies* instead of in the usual manner. The inverse wave-lengths of the chief rays in the spectra of magnesium, zinc, cadmium, copper, silver, silicon, boron, and aluminium have been mapped. In cases where measurements have not been made independently of the visible rays, I have availed myself of M. Lecoq de Boisbaudran's numbers and calculated the reciprocals therefrom. In every case independent calculations were made, though some of the

numbers might have been taken from the British Association Catalogue of Oscillation Frequencies of Solar Rays (Dublin Report, 1878, p. 40). In this catalogue a small correction, varying with the refrangibility of the rays, is applied to the reciprocals to eliminate the effect caused by the dispersion of air at 760 mm. barometric pressure, and a temperature of 16° C. Generally speaking, the first four figures are not affected by this correction.

The following are the descriptions of the several spectra. The lettering of the groups refers to the mass. Single lines are generally denoted by A and α , and when they recur they are distinguished by affixed numbers. Groups of lines, as pairs or triplets, are denoted by b , or b^1 , b^2 , and so on. An interval of 10 oscillations corresponds with the space of a millimetre, and the drawing is made with sufficient care as to indicate an interval between two lines equivalent to a difference of only one wave per millimetre, as for instance in the case of the boron, 4004 and 4005.

All lines included between 1500 and 2250 have been the subject of previous investigation, as they are within the range of the visible spectrum; beyond this upper limit lie the ultra-violet rays. Two maps have been published of the spectra of this region, namely, that of Mascart, of the cadmium lines (*Annales de l'École Normale*, 1864), and that of Liveing and Dewar, of the magnesium spectrum (*Proc. Roy. Soc.*, **32**, 189), both on the scale of wave-lengths.

THE MAGNESIUM SPECTRUM.

Table of Oscillation Frequencies.

The series of triplets—	A pair—
Oscillation frequencies.	Oscillation frequencies.
(1.) 1928·9 } (2.) 1932·9 } (3.) 1934·5 }	3412·8 } 3415·0 } c .
(1.) 2605·5 } (2.) 2609·9 } (3.) 2611·9 }	Single lines— 1809 a^1 2232 a^2 *3507 a^3
(1.) 2997·1 } (2.) 3001·0 } (3.) 3003·0 }	
(1.) 3228 } (2.) 3234 } (3.) 3236 }	

* Concerning this line 3507 a^3 ($\lambda = 2851\cdot3$, Hartley and Adeney, or 2852, Liveing and Dewar) the following observation has been made: "The great line of magnesium at wave-length 2852 certainly seems a fundamental one, if we may judge by

Intervals between the oscillation frequencies of the first, second, and third vibrations in the groups b^1 and b^2 , b^2 and b^3 , b^3 and b^4 respectively:—

	(1.)	(2.)	(3.)
Differences b^1 and b^2	677·1	677	677·4
„ b^2 and b^3	391·2	391·1	391·1
„ b^3 and b^4	230·9	233	233

Interval between individual lines in the four series of triplets:—

b^1 .	b^1 .	b^2 .	b^2 .
1934·5 (3)	1932·9 (2)	2611·9 (3)	2609·9 (2)
1932·9 (2)	1928·9 (1)	2609·9 (2)	2605·0 (1)
<hr/>	<hr/>	<hr/>	<hr/>
1·6	4·0	2·0	4·9
b^3 .	b^3 .	b^4 .	b^4 .
3003 (3)	3001 (2)	3236 (3)	3234 (2)
3001 (2)	2997 (1)	3234 (2)	3228 (1)
<hr/>	<hr/>	<hr/>	<hr/>
2	4	2	6

The quadruple group—

Oscillation frequencies.	
(1.) 3569	} <i>d.</i>
(2.) 3575	
(3.) 3578	
(4.) 3584	

The quintuple group—

Oscillation frequencies.	
(1.) 3594	} <i>e.</i>
(2.) 3596	
(3.) 3598	
(4.) 3601	
(5.) 3602	

its persistence, strength, and facility of reversal." ("On Circumstances producing the Reversal of Spectral Lines," *Proc. Camb. Philos. Soc.*, 4, Part 5, 265.) This remark seems to apply more particularly to the arc spectrum, for the strongest and most persistent lines observed when a condensed spark is used are those with wavelengths 2801·6 and 2794·1, the first and third of the quadruple group. If α^3 is a fundamental vibration of the magnesium molecule, it is remarkable that there is an absence in the zinc and cadmium spectra of any line corresponding to it.

THE ZINC SPECTRUM.

Oscillation frequencies. 1571 a single line.	Quadruple group—
Groups of triplets—	Oscillation frequencies.
(1.) 2079 } b^1 .	(1.) 4752 } d .
(2.) 2118 } b^1 .	(2.) 4757 } d .
(3.) 2136 } b^1 .	(3.) 4764 } d .
(1.) 2989 } b^2 .	(4.) 4771 } d .
(2.) 3028 } b^2 .	Quintuple group—
(3.) 3046 } b^2 .	(1.) 4795 } e .
(1.) 3571 } b^3 .	(2.) 4813 } e .
(2.) 3609 } b^3 .	(3.) 4834 } e .
(3.) 3629 } b^3 .	(4.) 4848 } e .
A pair—	(5.) 4852 } e .
3910 } c .	
3997 } c .	

Intervals between the first, second, and third lines in groups b^1 , b^2 , b^3 of zinc:—

Oscillation frequencies.		
(1.)	(2.)	(3.)
2989	3028	3046 b^2
2079	2118	2136 b^1
910	910	910

Oscillation frequencies.		
(1.)	(2.)	(3.)
3571	3609	3629 b^3
2989	3028	3046 b^2
582	581	583

Intervals between the individual lines in the groups b^1 , b^2 , b^3 of zinc:—

b^1 .	b^1 .	b^2 .	b^2 .	b^3 .	b^3 .
(3.) 2136	(2.) 2118	(3.) 3046	(2.) 3028	(3.) 3629	3609
(2.) 2118	(1.) 2079	(2.) 3028	(1.) 2989	(2.) 3609	3571
18	39	18	39	20	38

It is worthy of remark that the difference between the groups b^1 and b^2 + that between b^3 and b^4 in the magnesium spectrum, yield the number 910, the difference between groups b^1 and b^2 of zinc. Only by taking great care can the extreme groups of rays d and e in the

spectrum of zinc be photographed. Films particularly sensitive to the rays in this region may be prepared, upon which they may be photographed without difficulty.

THE CADMIUM SPECTRUM.

In the cadmium spectrum two lines, numbered by M. Mascart 9 and 10, are in reality double lines, with some measurable distance in wave-length. Then taking the wave-lengths of the two lines constituting No. 9 as 3612.5 and 3610, we have for the number of oscillations occasioned by each ray 2765 and 2770. The wave-length adopted for No. 10 are 3467.4 and 3465.7, giving for the oscillation frequencies 2884 and 2882.

<p>A single line—</p> <p style="padding-left: 2em;">Oscillation frequencies.</p> <p style="padding-left: 4em;">1553 <i>a</i>.</p> <p>A pair—</p> <p style="padding-left: 2em;">3639 } <i>c</i>.</p> <p style="padding-left: 2em;">3809 }</p> <p>Triples—</p> <p style="padding-left: 2em;">(1.) 1966 } <i>b</i>¹.</p> <p style="padding-left: 2em;">(2.) 2083 }</p> <p style="padding-left: 2em;">(3.) 2138 }</p> <p style="padding-left: 2em;">(1.) 2765—2770 } <i>b</i>².</p> <p style="padding-left: 2em;">(2.) 2884—2882 }</p> <p style="padding-left: 2em;">(3.) 2938 }</p> <p style="padding-left: 2em;">(1.) 3355 } <i>b</i>³.</p> <p style="padding-left: 2em;">(2.) 3472 }</p> <p style="padding-left: 2em;">(3.) 3525 }</p>	<p>Quadruple group—</p> <p style="padding-left: 2em;">Oscillation frequencies.</p> <p style="padding-left: 4em;">(1.) 4292 } <i>d</i>.</p> <p style="padding-left: 4em;">(2.) 4307 }</p> <p style="padding-left: 4em;">(3.) 4322 }</p> <p style="padding-left: 4em;">(4.) 4334 }</p> <p>Quintuple group—</p> <p style="padding-left: 2em;">(1.) 4369 } <i>e</i>.</p> <p style="padding-left: 2em;">(2.) 4413 }</p> <p style="padding-left: 2em;">(3.) 4461 }</p> <p style="padding-left: 2em;">(4.) 4535 }</p> <p style="padding-left: 2em;">(5.) 4555 }</p>
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Intervals between the first, second, and third lines in the groups *b*¹, *b*², and *b*³ of cadmium :—

(1.)	(2.)	(3.)
2767.5	2883	2938 <i>b</i> ²
1966.0	2083	2138 <i>b</i> ¹
801.5	800	800
3355	3472	3525 <i>b</i> ³
2767	2883	2938 <i>b</i> ²
588	589	587

Intervals between the individual lines in the three groups of triplets in the spectrum of cadmium :—

b^1 .	b^1 .	b^2 .	b^2 .	b^3 .	b^3 .
(3.) 2138	(2.) 2083	(3.) 2938	(2.) 2883	(3.) 3525	(2.) 3472
(2.) 2083	(1.) 1966	(2.) 2883	(1.) 2767.5	(2.) 3472	(1.) 3355
55	117	55	115.5	53	117

THE SPECTRUM OF COPPER.

Oscillation frequencies.

1906	} α^1 . Pair.
1959	
3054	} α^2 . Pair.
3079	
3675	} β -Group.
3678	
3685	
3700	
3703	
3719	
3929	} γ -Group.
3954	
3958	
3990	
4013	
4020	

THE SPECTRUM OF SILVER.

Oscillation frequencies.

1830	} α^1 . Pair.
1919	
2985	} α^2 . Pair.
3051	
3404	} β -Group.
3408	
3414	
3446	
3453	
3481	
3688	} γ -Group.
3759	
3765	
3805	
4032	
4037	
4043	

THE SPECTRUM OF ALUMINIUM.

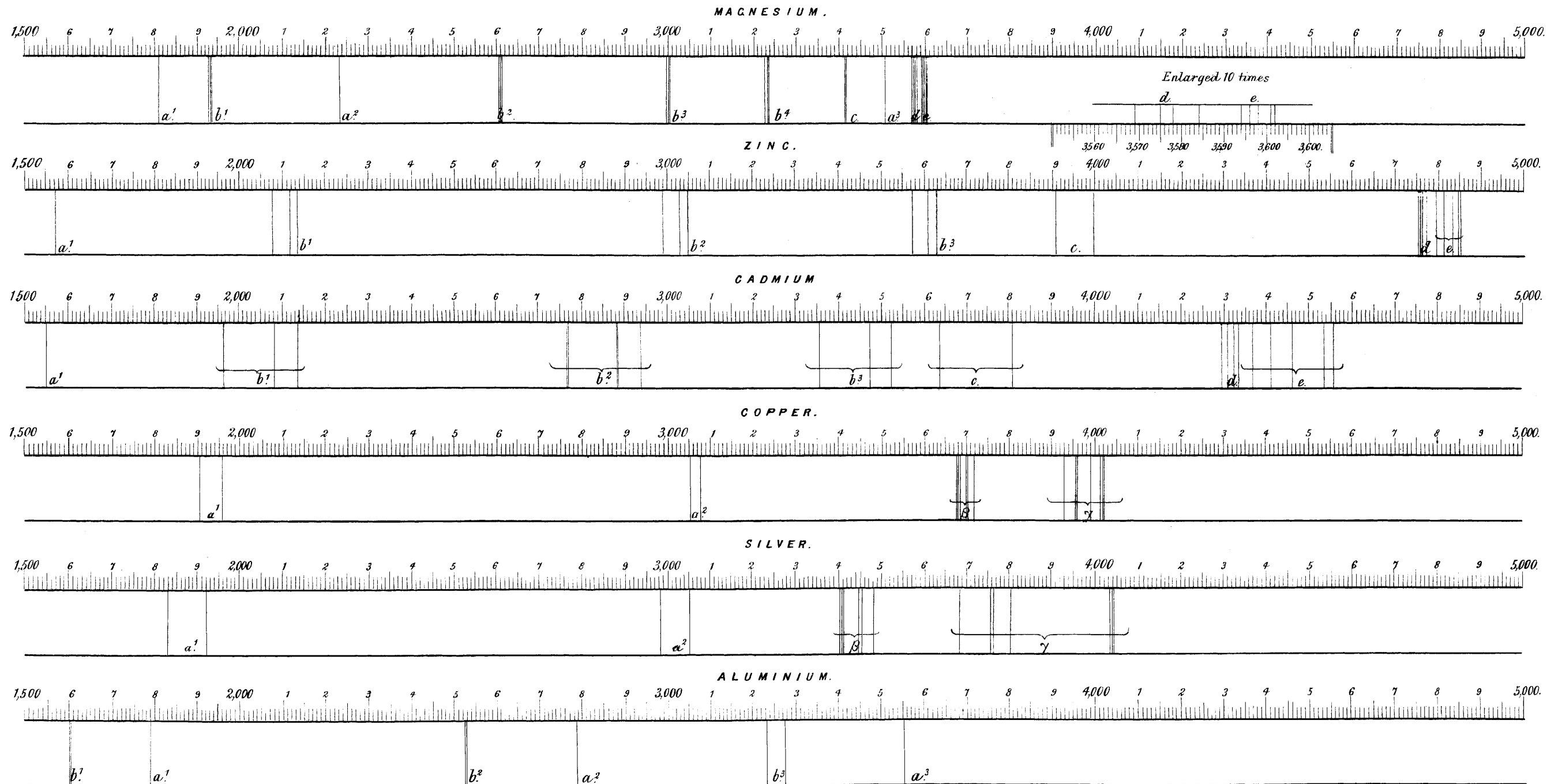
A spectrum of the second order, taken from solutions and from metallic electrodes:—

Oscillation frequencies.

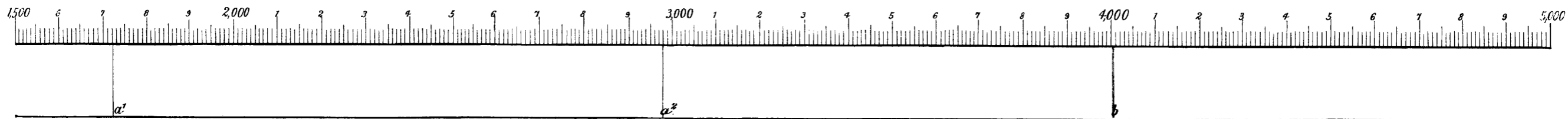
	(1.) 1601	} Pair b^1 .	
	(2.) 1603		
Difference	(1.) 924.		1788 a^1 . Isolated ray.
	(2.) 927.		
	(1.) 2525	} Pair b^2 .	Difference 1002.
	(2.) 2530		
Difference	(1.) 708.		2790 a^2 . Isolated ray.
	(2.) 747.		
	(1.) 3233	} Pair b^3 .	Difference 762.
	(2.) 3277		
			3552 a^3 . Isolated ray.

The pair b^2 are the aluminium lines lying between I + and K on M. Cornu's map of the solar spectrum. There are some lines of greater refrangibility than those given above, which, however, are readily

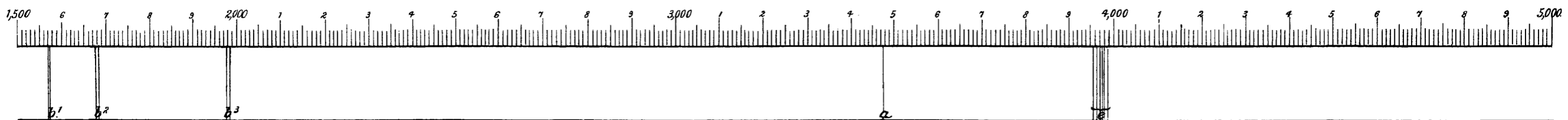
SPECTRA MAPPED ACCORDING TO OSCILLATION FREQUENCIES

Journ. Chem. Soc. Sep^r 1883.

BORON



SILICON



absorbed by air (Cornu, *Archives des Sciences Physiques et Naturelles* [3], 2, 112—126).

The intervals between the lines of the quintuple groups of magnesium, zinc, cadmium, and silicon are the following:—

Mg.	Zn.	Cd.	Si.
2	18	44	8
2	21	48	8
3	14	74	7
1	4	20	12

A relationship is observable between the Mg and Cd, but not between the other elements; doubtless more accurate determinations of these measurements are required.

THE SPECTRUM OF BORON.

To ascertain the relation of the spectrum of the 2nd Order of boron to those of beryllium and magnesium, borax in strong solution was submitted to the action of a condensed spark, and photographs of its spectrum were observed. The lines are strong and well marked, and apparently all of equal intensity. The least refrangible ray in the map is taken from Schützenberger's *Traité de Chimie Générale*, 1, 508.

Oscillation frequencies.

1721	a^1 .	An isolated ray.
2898	a^2 .	An isolated ray.
4004	} b .	A pair.
4005		

THE SPECTRUM OF SILICON.

The spectrum of silicon of the 2nd Order was obtained by taking sparks from a strong solution of sodium silicate, and photographing the rays. In addition to the lines mapped out, others of unequal intensity have been identified with silicon. The object in observing silicon was to verify if possible the statement of Ciamician concerning the compound nature of its spectrum and the relation of boron, beryllium, and carbon, to aluminium, magnesium, silicon, and oxygen. In addition to this spectrum three pairs of visible lines have been observed (Schützenberger, *Traité de Chimie Générale*, 1, 536), and these also are inserted in the map.

Pairs—	Oscillation frequencies.
	3471 a^1 . An isolated ray.
	3800 a^2 . An isolated ray.
1570 } b .	3935 } e . A fine group.
1574 } b .	3955 }
1668 } b^2 .	3962 }
1675 } b^2 .	3970 }
1977 } b^3 .	3975 }
1984 } b^3 .	3978 }
	3990 }
	4105 a^3 . An isolated ray.

The foregoing data present a considerable addition to the body of evidence in support of the view that elements whose atomic weights differ by a constant quantity, and whose chemical character is similar, are truly homologous, or in other words, are the same kind of matter in different states of condensation. It will be remembered that Mr. Norman Lockyer (*Proc. Roy. Soc.*, **28**, 157) has proposed to explain the occurrence of several coincident lines in the spectra of different elements by supposing that each spectrum is composed of several spectra, and that these compound spectra are the spectra of compound bodies, and not of elements. The action of a low temperature causes the vibration of a compound molecule, while the action of a high temperature causes a breaking up of the molecule either into smaller molecules of the same element, or into those of distinct elements. It appears also from the way in which he has treated the subject, that every elementary substance may be decomposed into as many simple substances as there are rays in its spectrum. I allude here to the observations concerning the lines in the spectra of iron, calcium, magnesium, lithium, and hydrogen. M. Lecoq de Boisbaudran (*Compt. rend.*, **73**, 943; and **82**, 1264), also Vogel (*Ber.*, **13**, 274), and Van Monckhoven (*Compt. rend.*, **95**, 520), have disposed of some of these facts upon which this theory is founded. With even very moderate dispersive power, something like 1200 lines can be recognised in the spectrum of iron, an element which has an atomic weight of 56, and it is simply inconceivable that a body of the chemical nature of iron can have a molecular structure so complex as to be composed of 1200 different simpler substances. Mr. Lockyer's hypothesis seems quite incompatible with the theory that the spectra are composed of harmonic vibrations, because a compound body would give two or more series of harmonics related to two or more fundamental vibrations, and elements having a common component should give spectra in which the same series or groups of lines should appear. If therefore we are to draw inferences as to the compound nature of substances from coincident lines in their spectra, it is not single lines but harmonic

series that we must look to for coincidences. I will give an illustration of this reasoning as applied to the spectra of tellurium and copper, in which appear the following lines:—

Copper.	Tellurium.
Wave-lengths.	Wave-lengths.
3307·4	3307·5
3290·2	3290·0
3280·5	3280·4 (very strong)
3273·6 (very strong)	3273·8 (very strong)
3264·3	3264·4
3247·3 (very strong)	3247·2 (very strong)

It is impossible to say whether these lines are coincident or not, as we cannot feel certain of the correctness of our measurements to 0·1-tenth meter, though they are believed to be correct to 0·2. It appeared at first sight that the copper contained tellurium, which it was impossible to separate; but this was soon seen not to be the case, because of two of the longest and strongest lines, 3280·4 and 3382·7, in the tellurium spectrum; the former was represented by a comparatively very weak line, and the latter was not represented at all. If copper, on the other hand, were contained in tellurium, either as a constituent of the element or as an impurity, the pair of lines α^2 should be followed by the groups β and γ , or preceded by α^1 . It is upon the recurrence of such groups of lines in spectra that Ciamician has based his conclusion that silica is composed of carbon and oxygen, with a corresponding atomic weight, $12 + 16 = 28$, and aluminium of boron and oxygen, $11 + 16 = 27$ (*Berichte der Kaiserlichen Akademie, Wien*, **72**, 139–44, 1880). It is to be regretted that Dr. Ciamician's maps of spectra refer to an arbitrary scale and not to wave-lengths, as several of the groups of lines which he has drawn appear to recur in the ultra-violet region; for example, the group which he designated by b in tellurium, and several in arsenic and antimony. It is doubtful whether the group of lines belonging to silicon which I have mapped is homologous with a somewhat similar group belonging to Ciamician's spectrum of silicon.

The probability of many of the fundamental vibrations of the simpler elements being found in the infra-red region will no doubt soon be put to the test of experiment, since we have Captain Abney's method of photography applied to these rays, and Professor Rowland's method of spectrum analysis by means of concave ruled specula, unequalled for dispersion and exquisite definition, giving us a range of at least four octaves. Professor Langley has shown that there are two octaves of vibrations below Λ (*Archives des Sciences Physiques et Naturelles*, **9**,

95, January, 1883), and M. Cornu has photographed lines of aluminium one octave above wave-length 3700. I hope in a future communication to return to this subject.
