IV. *On Relations between the Lines of various Spectra, with Special Reference to those of Cadmium and Zinc, and a Redetermination of their Wave-lengths.* By JOSEPH SWEETMAN AMES, Assistant in Physics, Johns Hopkins University.*

IN this paper I shall give a sketch, as complete as possible, of the many theories which have been advanced concerning spectral relations, with a short statement as to their agreement with the most recent investigations; and then I wish to call attention to a few new relations suggested by my own studies.

Relations between Different Spectra.

Alex. Mitscherlich† was the first, apparently, to seek numerical relations between the spectra of different substances. Having proved, independently of Roscoe, that the spectra of compounds were different from those of the elements themselves, he examined and compared the spectra of the haloid salts of barium, calcium, and strontium. He selected certain lines in each as most prominent, and found in the case of the salts of barium that the distance apart of these lines was directly proportional to the atomic weight of the salts themselves, while in the calcium and strontium salts the proportionality was an inverse one. He could find no relations in the spectra of the elements. Those found in the compounds were chance ones; for, using a prism spectroscope, his wave-lengths are arbitrary. A few years later, Mascart‡ called attention to the series of doublets in the spectrum of sodium and to one of triplets in the spectrum of magnesium. He thought there was some connexion between the relative distances of the lines in these similar groups, which could not be attributed to chance, and which might point to some "harmonic" relations.

In the same year M. Lecoq de Boisbaudran§ announced, as the result of his study of the flame-spectra of the alkalis and the alkaline earths, a simple law. He selected certain lines in each spectrum, which he called "homologous," as they appear (with certain changes) in the spectra of homologous substances, such as barium, calcium, and strontium. These lines do not, however, have the same wave-length in the different spectra; and his law was that the heavier the mole-

* Communicated by the Author.

† *Pogg. Ann.* cxxi. (1864); *Phil. Mag.* September 1864.

‡ *Comptes Rendus*, lxi. (1869).

§ *Tom. cit.*

cule of the element, the more were these lines shifted towards the red end of the spectrum. The main objection to all this is that until recently the selection of homologous lines has been a purely personal matter: any observer has had the privilege of calling "homologous" any lines he saw fit; and even now, as I shall show, it is mainly in the ultra-violet part of the spectrum that homologous lines and series can be definitely determined. To verify his law, M. de Boisbaudran takes the average of wave-lengths lying often far apart. This process can be justified only when each line separately obeys the law. But far more important than this relation is one which M. de Boisbaudran deduced some years later*. He states it as follows:—

"In the natural families (of elements), the variation in the increment of atomic weights is proportional to the variation in the increment of the wave-lengths of homologous rays (or groups of rays) in the 'third harmonic' of the spectra."

I cannot better explain the meaning of his terms than by giving in detail the application of the law to the determination of the atomic weight of germanium†.

Aluminium, gallium, and indium belong to the same "natural family;" and their atomic weights and spectra are known, so the ratio of the "variations in the increments" can be determined once for all. The average of the wave-lengths of a prominent pair of aluminium lines is, according to him, 3952; and homologous pairs in the spectra of gallium and indium give similarly 4101 and 4306. He takes as the atomic weights of the three metals 27·5, 69·9, and 113·5 respectively.

Hence we have:—

	λ .	$\Delta\lambda$.	$\Delta^2\lambda$.	Variation in Increment.
Al.	3952			
		149		
Ga.	4101		56	$\frac{56}{149} = \cdot 37584$
		205		
In.	4306			
Atomic weight.				
Al.	27·5			
		42·4		
Ga.	69·9		1·2	$\frac{1·2}{42·4} = \cdot 0283$
		43·6		
In.	113·5			

* *Comptes Rendus*, cii. p. 1291 (1886).

† *Ibid.*

Then, the ratio of these variations,

$$\frac{\cdot 37584}{\cdot 0283} = 13\cdot 28,$$

must be a constant for all the natural families.

The spectrum of germanium is partially known ; and it can be shown chemically that it belongs to the same family as silicon and tin. So, treating its atomic weight as an unknown quantity, and assuming certain values for the wave-lengths and atomic weights of silicon and tin, we have :—

	λ .	$\Delta\lambda$.	$\Delta^2\lambda$.	"Variation."
Si.	4010			
		443		
Ge.	4453		181	$\frac{181}{443} = \cdot 4051$
		624		
Sn.	5077			

Atomic weight.

Si.	28			
		$x - 28$		
Ge.	x		$146 - 2x$	$\frac{146 - 2x}{x - 28} = X$
		$118 - x$.		
Sn.	118			

By his law,

$$\frac{\cdot 4051}{X} = \frac{\cdot 37584}{\cdot 0283} = 13\cdot 28,$$

$$\therefore X = \cdot 03051,$$

$$\therefore x = 72\cdot 32.$$

So M. de Boisbaudran succeeds in getting identically the same value for the atomic weight as Winckler afterwards found by chemical means. This is surely a wonderful confirmation of the law, if the lines assumed to be homologous are so in reality. It is true that the atomic weights of the elements are not known so accurately as to justify M. de Boisbaudran in attributing such exactness to his deductions ; and so the method ought not to be applied to the determination of atomic weights. But, if the law is correct, it may well serve to identify homologous lines. Let us apply it to the case of magnesium, zinc, and cadmium. The ratio of the "variations," which is a constant for all natural families, is not known more accurately than 13·0 ; but this will do very well for our purposes. The variation in the increment of the

atomic weights of magnesium, zinc, and cadmium is $\cdot 146$. Hence the variation in the increment of the wave-lengths is $\cdot 146 \times 13 = 1\cdot 898$. I have recently studied the spectra of zinc and cadmium with much care; and, as will be shown later, each line in the one spectrum has an homologous one in the other. Two of these lines have the wave-lengths 2800·9 and 2980·8 respectively. This law of M. de Boisbaudran should enable us to find the corresponding line in the magnesium spectrum. Calling it x , the variation in the increment is

$$\frac{x - 2621\cdot 0}{2800\cdot 9 - x}$$

But this must equal 1·898. Hence $x = 2738\cdot 8$. In reality there is a line 2736·9; but its physical properties do not correspond to those of the two zinc and cadmium lines. Two other lines of zinc and cadmium, which are undoubtedly homologous, are 3345·1 and 3610·6; and the hypothetical magnesium line corresponding to these would have the wave-length 3253·6. There is, however, no line in this neighbourhood which can possibly be homologous with the zinc and cadmium lines. Therefore, while this law may apply roughly to certain lines, it surely cannot be considered general.

After M. de Boisbaudran several investigators, including Ditte and Troost and Hauteville*, endeavoured to trace relations between atomic weights and "displacement" of the spectra. But, as remarked above, it was impossible at this time to make any accurate statements as to homologous lines or their displacement. This fact is clearly shown by the disagreement of observers of the same spectra in regard to homologous lines. Cimician† examined the spectra of a great many substances in search of lines, and tried by a study of them to prove the compound nature of the elements. The dispersion of his instrument was, however, so feeble that he could not properly decide upon similarities in different spectra. He opposes M. de Boisbaudran's law of the shifting of the spectra, and says that instead of increasing with the atomic weight the wave-lengths increase with the intensity of the "chemical kinetic energy." (See Mohr, *Mech. Th. der Chem. Affinität*, Wien, 1867.) The first really scientific work on the relations between the lines of spectra was that of Hartley‡. In studying the spark-spectra of the elements, his attention was attracted to the many points of resemblance between the spectra of chemically similar elements, notably magnesium,

* *Comptes Rendus*, lxxii. (1871).

† *Wien. Sitzber.* 1877, 1878, 1880.

‡ *Journ. Chem. Soc.* 1882, 1883.

zinc, and cadmium. But it is hardly safe to draw inferences from spark-spectra; for, although they are undoubtedly characteristic, yet the state of affairs in the spark-discharge is so unnatural, if I may use the term, that similar molecules could not be expected to act alike. The study of the arc-spectra of the elements leads to many modifications and additions, as will be shown later. Prof. Hartley called attention also to a most remarkable relation connecting the lines in the series of triplets in the spectra of magnesium, zinc, and cadmium. He corrected the wave-lengths for atmospheric refraction, and then calculated their reciprocals; that is, he deduced quantities proportional to the frequencies of the waves. He then found that the differences of these frequencies for each triplet in any one series is a constant quantity. This law holds also for series of doublets. I will return to this point when the spectra of cadmium and zinc are discussed. That there are mathematical expressions connecting the many series of rays in the spectra of the elements no one can doubt. Their regularity and analogy are evidently not accidental. But there are two ways of arriving at such a mathematical formula: one is to deduce it from theoretical considerations and to test it by experiment; the other is to give up all preconceived ideas and simply to "guess," as Kepler did. Cornu* advises the latter method. He thinks that relations are to be found, if at all, between the lines which are "reversed." It is true that most of the lines in these series which obviously obey some common law are reversed; but different observers are continually finding different reversals. The conditions must be specified. While studying, then, the reversed lines of aluminium and thallium, Cornu noticed the resemblance between the series which they formed and the one of hydrogen lines. He thought he could trace a linear relation between them. That is, for all the ultra-violet reversed lines of aluminium (and of thallium) the following formula held:—

$$\lambda = a + b \lambda_1,$$

where λ_1 is the wave-length of one of the lines in the hydrogen series, beginning with wave-length 4340. That this formula is not true will be shown later when the wave-lengths of the aluminium lines are given.

In the spectra of zinc and cadmium some new points of resemblance were noted by Mr. Bell † quite recently; but he worked with the spark-spectra, and so was at a disadvantage. For the sake of completeness some notice must be taken of

* *Comptes Rendus*, c. (1885).

† *Amer. Journ. Sci.* [3] xxxi. (1886).

the recent attempt by Prof. Anton Grünwald * of Prague to deduce a mathematical theory of spectra and spectral relations. A synopsis of his theory and the objections to it have been given by myself †, and later by Kayser ‡. In his last paper Prof. Grünwald claims to find coincidences between lines in the spectra of antimony, tellurium, and copper, and then to deduce the proof of a new element. In fact, there is not a single coincidence between these three spectra. It is evident from his writings that Prof. Grünwald has never had the benefit of using and working with a spectroscope.

Harmonic and Combinational Lines.

There has been an attempt to solve the question of the origin of lines in spectra, which is quite different from the theories and relations already discussed. Since the motion imparted to the æther and known to us as light is a periodic one, it seems but natural to apply Fourier's series and to see if the presence of the various harmonics of the fundamental can be found. The first to find such simple relations was M. Lecoq de Boisbaudran §. He thought that line for line the two visible bands of nitrogen were related to each other in the ratio 3:4. Later and more accurate measurements have shown this relation to be inaccurate. Soon after Prof. G. Johnstone Stoney || pointed out some harmonic relations in the spectrum of hydrogen. At the same time he studied the absorption spectrum of CrO_2Cl_2 with a view to testing his theory; but the result was not satisfactory. At the best all the harmonics are never present; all the lines are not accounted for; and several fundamentals have often to be supposed. The ultra-violet lines of magnesium and cadmium were examined by Soret ¶ in the search for harmonic ratios; but his coincidences are very rough.

Liveing and Dewar ** also engaged in the quest for these harmonic relations in the spectra of lithium, sodium, and potassium, but with indifferent success. A few such relations can be found in every spectrum; but is this number greater than that which a chance-distribution would give? This question occurred to Schuster, while he was working on the spectrum of iron. He proposed the following problem:—

* *Astr. Nach.* p. 2797 (1887); *Wien. Sitzb.* 1887, 1888, 1889.

† *Amer. Chem. Journ.* xi. (1889); 'Nature,' xl. (1889).

‡ *Chem. Ztg.* xiii. pp. 1655 and 1687 (1889).

§ *Comptes Rendus*, lxi. (1869).

|| *Phil. Mag.* [4] xlii. (1871); 'Nature,' xxi. (1880).

¶ *Bibliot. Univ. Archives des Sci. Phys. et Nat.* Sept. 1871; *Phil. Mag.* [4] xlii. (1871).

** *Proc. Roy. Soc.* xxix. (1879); xxx. (1880).

“ Given n quantities distributed arbitrarily between 1 and A , what is the probable number of quotients of two of these n quantities, which will be equal to $\alpha \pm \delta$, where δ is small ? ”

He finds* the probable number to be

$$\frac{n(n-1)(A^2\alpha^2-1)\delta}{(A-1)^2\alpha^2},$$

where $A \approx \frac{1}{\alpha^2}$. Applying this result to the spectrum of iron

he finds, on the whole, fewer harmonics actually present than the formula demands. His conclusion, however, is that the law of distribution, although a complicated one, may in special cases resolve itself into the harmonic one. Since this investigation of Schuster's, the search for harmonic ratios has nearly ceased ; but, giving a broadened meaning to the word, Liveing and Dewar† have called attention to certain “ harmonic ” relations in spectra. These are, the repetition of similar groups, a certain sequence in distance, and a law of physical quality such as intensity and clearness.

A more recent attempt to apply dynamical reasoning and formulæ to the spectra of the elements has been made by M. V. A. Julius‡. On dynamical grounds there should be, he thinks, present in spectra lines whose frequencies are the sums or differences of the frequencies of other lines (the combinational tones of Helmholtz). So he deduces the probable number of coincidences, within limits $\pm \delta$, if the differences are taken between each two of n quantities lying at random between P and Q. He then actually calculates the differences in the case of eight spectra, and finds more coincidences than his formula says mere chance would give him. This theory of combinational rays would account also for the regularity of doublets and triplets, which was first noticed by Hartley, but which M. Julius apparently rediscovered. Until the wavelengths of the lines in the various spectra are known much more accurately than they are at present, such work as this is almost thrown away. The objective existence of combinational tones is now generally acknowledged, however ; and we may certainly expect corresponding phenomena in light-waves. This idea is not a new one ; but M. Julius is the first to elaborate it. In doing so, however, he neglects too much, I think, the physical properties of the lines. We would expect the strongest lines, if any, to be the ones to produce combina-

* Proc. Roy. Soc. xxxi. (1881).

† Phil. Trans. clxxiv. (1883).

‡ *Ann. de l'Ecole Polyt. de Delft*, 1889.

tional lines; but M. Julius gives equal importance to each line, faint or strong, hazy or sharp. The spectrum of calcium has some very strong lines in the red; and, as their wave-lengths have recently been carefully determined by Prof. Rowland, I thought I would test this theory by means of them. My search was in vain: not a combinational line could I find.

Distribution of Lines.

For many years spectroscopists have sought to reduce the distribution of lines in any one spectrum to a mathematical formula, but without much success. There are, however, one or two brilliant exceptions.

In 1885 J. J. Balmer* gave a formula for the lines in the hydrogen spectrum, which is most simple and which, as will be seen later, is remarkably accurate. His formula is

$$\lambda = \lambda_0 \frac{m^2}{m^2 - 4},$$

where λ_0 is a constant and m takes in succession the values 3, 4, 5.... More will be said of this formula when the hydrogen spectrum itself is discussed.

A formula was also advanced by Nordenskiöld†, the Arctic explorer; but it is quite inaccurate.

These two formulæ were found by trial; but it is interesting to note that one similar to Balmer's has been deduced theoretically. A general theory of radiation has been devised by Herr Kövesligethy‡, and in the course of this he arrives at the following wave-length formula:—

$$\lambda^2 = \mu_0^2 \frac{1}{R-1},$$

where μ_0 is the value of μ for the temperature of dissociation, μ being a function of the temperature and constitution of the body; and R is a function containing a parameter which must be determined for each substance. This formula is most suggestive; and the appearance of the elaborate treatise on the general theory, which is promised us, is eagerly expected.

In their first contribution to the "Spectra of the Elements"§ Kayser and Runge announce that they have found a general law for all spectra, which includes Balmer's as a special case. The uncertainty of the measurements of the

* Wied. *Ann.* xxv. (1885).

† *Comptes Rendus*, cv. (1887).

‡ *Astr. Nachr.* p. 2805 (1887); *Beibl.* xii. pp. 346 and 579 (1888).

§ *Abhd. Berlin Acad.* 1888.

wave-lengths of the elements is so great, though, that they have been unable to test it sufficiently. In a more recent paper* they give a formula for one of the cyanogen bands; but this is not, I judge, their general formula, nor even a special case of it.

The various bands found in the spectra of carbon and its compounds, and of many other substances also, seem at sight to be especially suitable for mathematical investigation; and many of them have been studied most carefully.

The first to hit upon an approximate law was Prof. A. S. Herschel† of Newcastle-on-Tyne. On seeing Piazzi Smyth's map of the green band of CO, which was plotted in wave-numbers or frequencies, he at once noticed that the differences of the lines were in arithmetical progression. This was in November 1883. He announced his intention of studying other bands; but I can find no record of his having done so. Prof. Rowland, independently, detected a similar law as soon as he began his work on the solar spectrum, which was in 1885. He investigated the A, B, and α bands first, and afterwards all the carbon bands. He found that the law was not so exact as the accuracy of his measurements demanded, and so never published his work.

Later on, M. H. Deslandres, working in Cornu's laboratory, came upon the same approximate law. Cornu‡ had noted that the reciprocals of the wave-lengths of the homologous lines in the three bands A, B, and α were nearly in arithmetical progression; and in his monograph on these telluric bands (Paris 1886) he says that the law of distribution of the doublets is sensibly the same in all three. This law, stated analytically, is

$$\frac{\Delta\lambda}{\lambda} = \frac{\Delta\lambda'}{\lambda'} = \frac{\Delta\lambda''}{\lambda''},$$

where $\Delta\lambda$, $\Delta\lambda'$, $\Delta\lambda''$ are the distances from the homologous lines to the "isolated" ones; and λ , λ' , λ'' are the averages of the rays whose intervals are $\Delta\lambda$, $\Delta\lambda'$, $\Delta\lambda''$. This law is only the roughest approximation. Cornu does not seem to have thought of testing the lines of each group separately. But in 1886 Deslandres§ published his investigation of the nitrogen bands; and stated that for all of them, and in fact for all bands so far examined, the following law is true:—"In general, the rays composing a band can be divided into

* *Abhd. Berlin Acad.* 1889; *Wied. Ann.* xxxviii. (1889).

† *Trans. Roy. Soc. Edinb.* xxxii. [3] (1884).

‡ *Comptes Rendus*, xcvi. (1884).

§ *Comptes Rendus*, ciii. (1886); also vol. civ. (1887), and vol. cvi. (1888).

several overlapping identical series ; and in each series the intervals from one ray to the next (measured in wave-numbers) form approximately an arithmetical progression." As Deslandres remarks, for most bands it is immaterial which we use, λ , $\frac{1}{\lambda}$, or $\frac{1}{\lambda^2}$; but $\frac{1}{\lambda}$ seems to apply most generally. In

a later paper Deslandres says that the bands themselves form groups, and that the same law governs the distribution of bands as governs the lines in any one band. Thus for any ray,

$$\frac{1}{\lambda} = Am^2 + Bm + C, \quad m = 0, 1, \dots$$

$$C = Dn^2 + En + F, \quad n = 0, 1, \dots$$

$$\therefore \frac{1}{\lambda} = Am^2 + Bm + Dn^2 + En + F.$$

Deslandres gives reasons for believing the general formula is of the form :—

$$\frac{1}{\lambda} = f(n^2, p^2) m^2 + Bn^2 + \phi(p^2).$$

This he compares with that of a vibrating rectangular prism, which likewise is a function of three positive parameters. These laws of Deslandres apply fairly well to all banded spectra ; but they are only approximations. I had made measurements of many of the bands of carbon and cyanogen to test their accuracy, but have been anticipated in their publication by Kayser and Runge*. They find, as I had done, that these laws fail in some cases. They study with particular care the most regular of the cyanogen bands, the one at wave-length 3883.5, and find that the empirical formula

$$\frac{1}{\lambda} = a + be^{cn} \sin(dn^2),$$

where a, b, c, d are constants and $n=0, 1, 2, \dots$ applies reasonably well. But in testing this formula they make no correction for atmospheric refraction, which would, I think, make some difference. They come to the conclusion that no exact formula, which is reasonably simple, can be found by trial. If one is ever to be known it must be deduced theoretically.

Some New Relations.

The two elements between whose spectra there is the most striking resemblance are, as is well known, zinc and cadmium.

* *Abhd. Berlin Akad.* 1889; *Wied. Ann.* xxxviii. (1889).

Their great similarity has often been noted ; but, as the spark-spectra have nearly always been studied, the exact correspondence between them has so far escaped notice. It is to be regretted, too, that in general so little attention has been paid to the physical properties of the lines, when homologous groups or series were selected. It is only, I think, by means of the physical similarities that correct inferences can be made. For these two reasons a great many of the relations given by Prof. Hartley are inaccurate. All of my measurements and descriptions of the zinc and cadmium spectra are taken from the photographs of the arc-spectra recently made by Prof. Rowland. My measurements are only provisional and do not possess a greater accuracy than 0.1 of a unit (*i. e.* $0.01\mu\mu$). This is sufficient for present purposes, and Prof. Rowland, who has nearly completed a systematic study of the spectra of the elements, will soon publish his tables of wave-lengths, which will be accurate to 0.01 of a unit. There will be noticed a discrepancy between my wave-lengths of cadmium and those given by Mr. Bell* The reason for this was discovered by Mr. Bell and myself, when we were working on the spark-spectrum of cadmium two years ago. A mistake of one unit in one of Mr. Bell's micrometer-readings vitiated one of the standard wave-lengths (which were used for the determination of the others). The scale of my wave-lengths is that of Rowland's map, as its superiority is now universally acknowledged. The wave-lengths are afterwards corrected for atmospheric refraction by means of interpolations in Ketteler's † determinations. These corrections become very uncertain in the extreme ultra-violet ; but no better values are known.

Zinc.

Wave-length in Air.	Wave-length in vacuo.	Wave-numbers.	
6362.5	6364.4	$1571.2 \pm .02$	
4810.7 r. } α .	4812.2	$\left\{ \begin{array}{l} 2078.0 \pm .04 \\ 2117.0 \\ 2136.0 \end{array} \right.$	Strong and sharp.
4722.3 r. }	4723.7		
4680.3 r. }	4681.7		
4630.1	4631.5	$2159.1 \pm .05$	
3346.2	3347.3	$\left\{ \begin{array}{l} 2987.5 \pm .09 \\ 2987.9 \\ 2988.5 \end{array} \right.$	Very strong and nebulous.
3345.7	3346.8		
3345.1 r. } β .	3346.2		
3303.1	3304.2	$\left\{ \begin{array}{l} 3026.4 \\ 3026.8 \\ 3045.6 \end{array} \right.$	
3302.8 r. }	3303.8		
3282.35 r. }	3283.4		

* Amer. Journ. Sci. [3] xxxi. (1886).

† Phil. Mag. [4] xxxii. (1866).

Zinc (*continued*).

Wave-length in Air.	Wave-length in vacuo.	Wave-numbers.	
3076.1 r.	3077.1	$3249.8 \pm .11$	
3072.1 r. } γ .	3073.1	$\left\{ \begin{array}{l} 3254.0 \\ 3292.8 \\ 3311.8 \end{array} \right.$	Sharp.
3035.9	3036.9		
3018.5	3019.5		
2800.9 r. d. } δ .	2801.8	$\left\{ \begin{array}{l} 3569.1 \pm .13 \\ 3607.8 \\ 3626.6 \end{array} \right.$	Strong and nebulous.
2770.9 r. d.	2771.8		
2756.5 r.	2757.4		
2712.6	2713.5	$\left\{ \begin{array}{l} 3685.3 \pm .14 \\ 3724.3 \\ 3743.1 \end{array} \right.$	Sharp and faint.
2684.2	2685.1		
2670.7	2671.6		
2608.7	2609.6	$\left\{ \begin{array}{l} 3832.0 \pm .15 \\ 3870.9 \\ 3889.7 \end{array} \right.$	Strong and nebulous.
2582.5	2583.4		
2570.0	2570.9		
2516.2	2517.0	$\left\{ \begin{array}{l} 3973.0 \pm .16 \\ 4012.2 \\ 4031.1 \end{array} \right.$	Nebulous.
2491.6	2492.4		
2479.9	2480.7		
2463.7	2464.5	$\left\{ \begin{array}{l} 4057.6 \pm .17 \\ 4096.3 \\ 4115.6 \end{array} \right.$	Hazy.
2440.4	2441.2		
2429.0	2429.8		
2138.3 r.	2139.0	$4675.1 \pm .22$	

This last line is a broad reversal.

Cadmium.

Wave-length in Air.	Wave-length in vacuo.	Wave-numbers.	
6438.8	6440.7	$1552.6 \pm .02$	
5086.1 r. } α .	5087.6	$\left\{ \begin{array}{l} 1965.6 \pm .05 \\ 2082.7 \\ 2136.9 \end{array} \right.$	Strong and sharp.
4800.0 r.	4801.5		
4678.3 r.	4679.7		
4413.1	4414.5	$\left\{ \begin{array}{l} 2265.3 \\ 2765.7 \pm .08 \\ 2766.9 \end{array} \right.$	
3614.6	3615.7		
3613.1	3614.2		
3610.6 r. } β .	3611.7	$\left\{ \begin{array}{l} 2768.8 \\ 2882.8 \\ 2884.1 \end{array} \right.$	Very strong and nebulous.
3467.7	3468.8		
3466.15 r.	3467.3		
3403.7 r.	3404.8	$\left\{ \begin{array}{l} 2937.0 \\ 3065.4 \pm .09 \\ 3073.5 \pm .10 \end{array} \right.$	
3261.1 r.	3262.2		
3252.6 r.	3253.6		
3133.2	3134.2	$\left\{ \begin{array}{l} 3190.6 \\ 3244.7 \\ 3353.7 \pm .12 \end{array} \right.$	Sharp.
3081.0	3082.0		
2980.8 r. d. } δ .	2981.8	$\left\{ \begin{array}{l} 3469.9 \\ 3523.7 \\ 3485.4 \pm .13 \end{array} \right.$	Strong and nebulous.
2881.0 r. d.	2881.9		
2837.0 r.	2837.9		
2868.2	2869.1	$\left\{ \begin{array}{l} 3602.4 \\ 3656.7 \\ 3616.9 \pm .14 \end{array} \right.$	Sharp and faint.
2775.0	2775.9		
2733.8	2734.7		
2763.9 d. } ζ .	2764.8	$\left\{ \begin{array}{l} 3733.4 \\ 3787.4 \\ 3757.7 \pm .15 \end{array} \right.$	Strong and nebulous.
2677.6 d.	2678.5		
2639.4	2640.3		
2660.3	2661.2	$\left\{ \begin{array}{l} 3874.3 \\ 3928.2 \\ 3841.7 \pm .16 \end{array} \right.$	Nebulous.
2580.2	2581.1		
2544.8	2545.7		
2602.1	2603.0	$\left\{ \begin{array}{l} 3958.7 \\ 4012.5 \end{array} \right.$	Hazy.
2525.3	2526.1		
2491	2492		
2288.1 r.	2288.9	$4368.9 \pm .19$	

This last line is a broad reversal; and 2980·8 is probably triple. As usual, “r” means reversed; and “d” double.

This list of lines does not pretend to include *all*; for a very few faint ones could not be measured as accurately as I wished.

The two spectra, as will be noticed, consist mainly of groups of three lines; these triplets overlap in the cadmium spectrum, but owing to the physical similarity of the lines forming any one triplet it was a matter of perfect ease to select them. Thus it is evident that line for line, group by group, the two spectra correspond. The only possible exception is in group ξ . In cadmium the first two lines are plainly double, while in zinc they are not resolved. The lines are broad and nebulous; and the zinc lines will, I think, be proved double. The more closely the two spectra are examined the more perfect does their agreement appear.

If we observe either spectrum, it is at once evident that groups β , δ , ξ , η , θ form a series. Taking the differences of the wave-numbers of the last lines in each of these triplets, we have for zinc:—

581·0, 263·1, 141·4, 84·5;

for cadmium:—

586·7, 263·7, 140·8, 84·3.

The correspondence is again evident. These series resemble greatly the series of hydrogen lines; and, as so many spectra have these series, it may be well to describe them in detail. These series always run in the same direction; that is, the relative distances of the lines grow smaller as the wavelengths become smaller. The lines forming the series are always nebulous; they are strong towards the red end, but rapidly become faint and hazy as we go down the series. The spectrum of the substance has, in general, other lines than those forming the series: the latter are the ones that always appear in the solar spectrum, the former ones may not. Their regularity is perfect. Returning to the zinc and cadmium spectra, and taking differences in wave-numbers between the first and second and the second and third lines of each triplet in the two spectra, excepting β and δ , we have:—

For zinc,

39·0	38·8	39·0	38·9	39·2	38·7
19·0	19·0	18·8	18·8	18·9	19·3

For cadmium,

117·1	117·1	117·0	116·5	116·6	117·0
54·2	54·1	54·3	54·0	54·1	53·8

Groups β and δ are excluded because, containing doublets and triplets, it is impossible to determine just what wave-number should be used.

It is difficult to say whether or not the agreement in the above figures would be better if the wave-numbers were known more accurately; but I am inclined to think that natural constants for the two metals are indicated by them.

It will be noticed that nearly all the homologous groups are in the ultra-violet. This seems to be true of all spectra. It is only, apparently, when the wave-numbers, or frequencies, are sufficiently large, that the similar modes of vibrations of the molecules become evident.

The resemblance of the spectrum of magnesium to those of zinc and cadmium is much less marked than the one just noted. In fact, I think nearly all the points of similarity given by Prof. Hartley are wrong. Magnesium has, it is true, ten groups of triplets; but their physical properties bear no apparent relation to those of the zinc and cadmium triplets. The beautiful series of five lines at wave-length 2779.9 in the magnesium spectrum surely has no companions in the zinc and cadmium spectra. There is, however, one striking feature common to all three. This is the presence of one broad reversed line. In magnesium it is at wave-length 2852.2; in zinc, at wave-length 2138.3; in cadmium, at wave-length 2288.1. Liveing and Dewar have observed the line at wave-length 2852.2 in the arc-, spark-, and flame-spectra of magnesium; so it is evidently in some sense a fundamental line. The differences of the wave-numbers in each magnesium triplet are also nearly constant, being close to 4 and 2.

The spectra of calcium, strontium, barium, and mercury also contain triplets; but their number is small in comparison with that of the lines not so included.

It is hardly necessary to refer to the series of pairs in the spectra of sodium, copper, and silver; but it may be well to note that each of these spectra has in the ultra-violet one prominent pair, always occurring as impurity lines, very "persistent," and coinciding with the solar spectrum. The sodium pair has the wave-length 3303.0 and 3302.4; that of copper, 3274.0 r. and 3247.7 r.; that of silver, 3282.9 r. and 3280.7 r. The presence of silver in the sun is at last proved. From a study of their physical properties I think the series of sodium pairs is in reality made up of two overlapping series, thus bearing a resemblance to the two series of potassium pairs.

The spectrum of lithium is similar to that of hydrogen. It has a series similar to the hydrogen one and obeying almost identically the same law, beginning at wave-length 3232.8.

In order to test Cornu's theory of the connexion between aluminium and hydrogen, I have measured with some care the wave-lengths of the aluminium pairs as photographed by Prof. Rowland. The wave-lengths of the hydrogen lines were determined by myself. Cornu's theory, stated concisely, is that for aluminium

$$\lambda = a + b \lambda_1,$$

where λ_1 is the wave-length of a hydrogen line. According to Cornu the following lines correspond :—

Al.	H.
2373·2	4340·66
2269·2	4101·85
2210·15	3970·25
2174·0	3889·15
2150·4	3835·6

If his theory is true, the ratios of the differences of each two consecutive lines should be the same for each series. Taking the first three lines of each, we find the ratio 1·76 for aluminium and 1·81 for hydrogen. The other ratios agree better ; but still the difference is too great.

As noted above in the historical sketch, the law that the second differences of the wave-numbers of the lines forming a band is constant, is approximately true. No general law more exact than this can, I think, be deduced with our present knowledge. But there seems to be some connexion between the lines forming a band and those in a series like the hydrogen ones : the former may be regarded as forming the "head" of this latter series. There is this true, however : the bands can run in either direction, towards the red or towards the ultra-violet ; while the series always turn one way. But, in spite of this, it may not be without use to show that the bands and the series are connected mathematically.

Balmer's law for the distribution of the hydrogen lines, stated in a slightly more general form, is :—

$$\frac{1}{\lambda} = a \left(1 + \frac{b}{c + m^2} \right), \quad m = 0, 1, 2 \dots$$

If we substitute in this

$$m = M - n, \quad n = 0, 1, 2 \dots,$$

where M is a constant many times as great as n , we have

$$\frac{1}{\lambda} = A + Bn + Cn^2 + \&c.,$$

where the coefficients rapidly grow smaller. This formula is, of course, the analytical statement that for lines near the head of a band the second differences of the wave-numbers are constant. So, if these series and bands represent in any degree the fundamental or original vibrations of the "molecule," as I think probable, it is of interest to note that a similar law applies to both. The exact law of distribution which must come from theoretical considerations will therefore include this as a special case.

Addendum.—Since writing the above the Philosophical Magazine for April (1890) has reached me, and it contains an article by Dr. Rydberg, of the University of Lund, "On the Structure of the Line-Spectra of the Chemical Elements," which demands notice. In this paper, which is only preliminary, Dr. Rydberg calls special attention to the many series in the spectra of the elements, divides them into various classes, gives formulæ for their distribution, and states that the wave-lengths are periodic functions of the atomic weights. This last relation, which is barely indicated in the article, seems to be nothing but the one of M. de Boisbaudran, which has already been discussed*. The law of distribution is nothing but Balmer's slightly generalized. The valuable part of the paper lies in the division of the lines of the spectra into different series and in showing the relations between them. He does not state how he gets his wave-lengths; but they seem to be a combination of Hartley's and Liveing and Dewar's. So he has confused the spark- and arc-spectra.

V. *On some Gaseous Spectra:—Hydrogen, Nitrogen.* By JOSEPH SWEETMAN AMES, Assistant in Physics, Johns Hopkins University†.

MY investigations on the spectra of gases were begun at the suggestion of Professor Rowland, and were designed primarily to ascertain the exact wave-lengths of the line-spectrum of hydrogen. Incidentally some other spectra have also been studied.

Method and Apparatus.

A concave grating, mounted in the well-known Rowland manner, was used. It was ruled especially for this research, was 6 inches (15.2 centim.) wide with 20,000 lines to the inch, and had a radius of curvature of 13.5 feet (4.11 metres).

The experiments were conducted according to the method

* Pp. 33 *et seq.*

† Communicated by the Author.