

# PROCEEDINGS

OF

## THE ROYAL SOCIETY.

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“A Comparative Study of the Spectra, Densities, and Melting Points of some Groups of Elements, and of the Relation of Properties to Atomic Mass.” By HUGH RAMAGE, B.A., A.R.C.Sc.I., St. John’s College, Cambridge. Communicated by Professor G. D. LIVEING, F.R.S. Received November 7,—Read November 28, 1901.

[PLATES 1, 2.]

### *Introduction.*

This investigation was begun in the hope that it would lead to the discovery of some of the laws which determine the distribution of lines and bands in spectra: those laws, more especially, which govern the changes of oscillation frequency of corresponding lines in the spectra of some of the metals.

A. Mitscherlich appears to have been the first to make a comparative study of spectra.\* He compared the spectra of the haloid salts of the metals of the alkaline earths. He found that individual lines recur in the spectra of one and the same metal, which, according to the halogens, are more or less distant from one another. Fluorides form an exception. In the spectra of barium compounds the distances (on the scale of his spectroscope) between two prominent lines in the various spectra were to each other as the “atomic weights” of the compounds. In barium chloride the distance between the two lines was 3·9 scale divisions. If  $x$  is the difference between the two corresponding lines in the spectrum of barium iodide, then :—

$$\frac{3\cdot9}{x} = \frac{104}{195\cdot5} = \frac{\text{BaCl}_2}{\text{BaI}_2}.$$

Mitscherlich determined a common starting point for the haloid salts of barium, and extended the work to the spectra of compounds of calcium and strontium.

\* ‘Pogg. Ann.,’ vol. 121, pp. 459—488, 1864; ‘Phil. Mag.,’ vol. 28, p. 169, 1864.

Lecoq de Boisbaudran,\* in proposing a theory on the origin of the spectral lines, made the following observations:—

“Les raies spectrales des métaux alcalins (et alcalinoterreux), classés par leur réfrangibilités, sont placées, comme les propriétés chimiques, suivant l'ordre des poids atomiques.”

“Le spectre du rubidium paraît donc alors analogue à celui du potassium, étant seulement transporté, comme tout d'une pièce, vers le rouge.”

Boisbaudran later (1870) laid stress upon these analogies, especially between the spectra of potassium, rubidium and caesium, but he made no reference to the spectra of lithium and sodium.

In 1886† he extended his comparative researches on spectra, and calculated the atomic weights of gallium and germanium from data supplied by their spectra and the atomic weights and spectra of other elements. Ames criticised this work,‡ and showed that the method failed when applied to other elements.

The discovery of harmonic series of lines in the spectra of elements by Liveing and Dewar,§ and the work of Hartley|| on “Homologous spectra,” indicated that there was a general law which applied to the production of the spectra of several elements. The formulæ which have been applied to these series, notably by Balmer, Kayser and Runge, and, more especially, the formula and work of Rydberg, have emphasised this fact in a most striking manner. Rydberg¶ discussed the spectra of the more common monad, dyad and triad metals very fully, and enunciated several important laws. His work will be considered in some detail in the course of this paper.

*Methods available for the Selection of the Corresponding Lines in Spectra.*

Ames, in discussing the difficulty of discovering these lines,\*\* said that the first really scientific work in this direction was done by Hartley's discovery of the constant differences of oscillation frequency between the members of doublets and triplets.††

Liveing and Dewar's harmonic series of lines, and the formulæ of Rydberg and of Kayser and Runge, give valuable assistance in this part of the work.

The author was led to *begin* this investigation by the knowledge of flame spectra which he acquired whilst working with Professor Hartley.

\* ‘Comptes Rendus,’ vol. 69, 1869.

† *Ibid.*, vol. 102, pp. 1291–5.

‡ ‘Phil. Mag.,’ 5th series, vol. 30, p. 47, 1890.

§ ‘Phil. Trans.,’ vol. 174, pp. 187–222, 1883.

|| ‘Trans. Chem. Soc.,’ vol. 43, p. 390, 1883.

¶ ‘Kongl. Svenska Vetensk. Akad. Handl.,’ vol. 23, No. 11, 1890.

\*\* ‘Phil. Mag.,’ vol. 30, 1890, p. 47.

†† ‘Trans. Chem. Soc.,’ vol. 43, p. 390–400.

Upwards of thirty metals yield spectra when heated in the oxyhydrogen flame: these metals also yield arc and spark spectra. The flame spectra are the simplest: the spark spectra are the most complicated.

Under the conditions which obtain in flames, the metals are usually heated to a temperature not very far removed from their boiling points, while the electrical conditions are probably simpler than obtain in the electric arc or spark. There are present in the Bunsen flame, in addition to the vapour of the metal, various gases such as: hydrogen, oxygen, oxides of carbon, steam and nitrogen, all heated to a high temperature. Some of the chemical changes which take place in the flame are reversible, and the metallic vapours are consequently in presence of gases, some of which are combining together, some are the compounds formed, and some of the latter are undergoing dissociation. Similar changes occur in the oxycoal-gas flame. The reactions in the oxyhydrogen flame are simpler, but similar spectra of metals are obtained from both of these high temperature flames.

It is possible, by varying the temperature of the flame, to obtain the simplest or fundamental spectra of many of the metals, and also to study the order of appearance of additional lines as more complex spectra are produced.

The metals of the alkalis and alkaline earths give spectra in the Bunsen flame. The former yield line spectra, the latter yield spectra composed of lines and bands. The bands and some of the lines have been attributed to the oxides of the metals. Indium gives a spectrum composed of two lines, and thallium a spectrum of one green line in the Bunsen flame. No other metals give spectra of importance in this flame.

Spark spectra of salt solutions, produced without the aid of a Leyden jar, are very similar to the arc and high temperature flame spectra of the metals present in those salts.

Flame spectra, then, furnish purely experimental data with which to begin an investigation of the laws which govern the distribution of the lines in spectra, and by which to study the relations of the physical and chemical properties of the metals to their spectra. Further experimental data are furnished in studying more complex spectra by:—

- (a.) The self-reversal of lines.
- (b.) The character of the lines—sharp or nebulous; continuous or discontinuous.
- (c.) Hartley's discovery of the constant differences between the oscillation frequencies of the components of doublets and triplets.
- (d.) The Zeeman effect.

- (e.) The effect on the lines of a change of atmosphere surrounding the source of light.\*
- (f.) Shift of lines under changes of pressure.†
- (g.) Harmonic series of lines.

The formulæ of Rydberg and of Kayser and Runge should be used in connection with the last of the above.

The experimental data are still incomplete, especially in the red, infra-red and ultra-violet regions. We now believe that the greatest accuracy of measurement and the fullest details of the ultra-violet lines are most necessary for the completion of this investigation. As far as can be seen from the data now available, all the above methods lead, and will lead, to the selection of the same lines as being produced by corresponding motions of or in the molecules. Much experimental work must yet be done, and it is hoped that the present investigation will indicate the direction and character of the work most needed.

### *Flame Spectra.*

*Bunsen Flame Spectra.*—Eder and Valenta have studied these over the greatest range of spectrum. They, by heating the chlorides of lithium, sodium, potassium, calcium, strontium, and barium in the Bunsen flame, obtained spectra composed of lines and bands, which they attributed to the metal, oxide, or chloride in each spectrum.‡

*Oxyhydrogen Flame Spectra.*—Hartley has studied these in the ultra-violet region and in the more refrangible portion of the visible spectrum.§ The author assisted Professor Hartley in this work, and from the summer of 1893 until 1899 the investigation was conducted as a joint work. The spectra of nearly all the elements were photographed in the course of the investigation: some of them gave only continuous spectra, and these cannot be included in the present work. Of the others, the following nineteen have been selected and studied in detail:—

- (1.) Lithium, sodium, potassium, rubidium, and caesium.
- (2.) Copper, silver, and gold.
- (3.) Magnesium, zinc, cadmium, mercury.
- (4.) Calcium, strontium, barium.
- (5.) Aluminium, gallium, indium, thallium.

The following metals also yield line flame-spectra, but the spectra have not been grouped as perfectly, nor studied as fully, as those of

\* Crew, 'Phil. Mag.,' November, 1900.

† Humphreys and Mohler, 'Astrophys. Jour.,' vol. 3, p. 114, 1896.

‡ 'Sitzber. Kais. Akad. Wien,' vol. 60, 1893.

§ 'Phil. Trans.,' A, 1894, 161–212.

the metals given above:—Tin, lead, bismuth, chromium, manganese, iron, cobalt, nickel, ruthenium, rhodium, palladium, and iridium.

The above nineteen metals may be\* classified by their spectra, as shown, into groups in agreement with Mendeléeff's Periodic Law. The spectra of the metals in each group are similar to one another, and they are quite different from the spectra of the other groups.

### *The Diagrams.*

It is apparent, when comparing the spectra of each group, that the positions of the strongest lines, and of the others in order, change regularly with the increase of atomic mass of the metals. The change in position is apparently so simple that it suggested a graphical method of representing the spectral lines as functions of the atomic mass. The lines were plotted as abscissæ, and the atomic masses as ordinates. Two diagrams were drawn at first, one from the oscillation frequencies of the lines, and the other from the wave-lengths. Connecting lines were then drawn through the corresponding lines in homologous spectra. These were mostly curved, and it was thought that the equations to these curves might be discovered by further study, and also that some relation might possibly be discovered between the equations.

Several curious results were obtained by observations on the points in which the converging lines, drawn through the corresponding members of doublets and triplets, intersected. These points were on the same horizontal line in each group, but it was difficult to determine their position accurately, and the results have since been regarded more as coincidences. The method, however, gave promise of yielding valuable results, and the research has been continued, partly by a further investigation of flame spectra and partly by an improvement in the method of drawing the diagrams. Use has been made also of some of the work of Rydberg, Preston, and others, to whom reference will be made in the paper, to make the research as accurate and complete as possible.

### *Discussion of the Spectra and the Lines.*

It may be stated at once that nearly all the lines observed in the flame spectra of the metals considered have been included in the diagrams. A few lines, selected from arc and spark spectra, have been used, but only in cases where our knowledge of flame spectra is incomplete.

There is no difficulty in selecting the corresponding lines from some spectra.

*Calcium, Strontium, Barium.*—The oxyhydrogen flame spectrum of each

\* Hartley and Ramage, 'Trans. Roy. Dublin Soc.,' N.S., vol. 7, pt. 12.

of these contains one line which is very much stronger than any of the other lines. The wave-lengths are:—Calcium 4227, strontium 4607, barium 5536. Eder and Valenta record them also in Bunsen flame spectra of the chlorides of these metals. They attribute the following lines to the *metals*:—

|                         | Intensity in— |              |        |
|-------------------------|---------------|--------------|--------|
|                         | Bunsen.       | Oxyhydrogen. | Arc.   |
| Calcium—<br>4227.....   | 10            | 10           | 10 $r$ |
| Strontium—<br>5968..... | 2             | —            | —      |
| 4608.....               | 10            | 10           | 10 $r$ |
| 4032.....               | 2             | —            | 46 $r$ |
| Barium—<br>6497.....    | 2             | 7            | 6 $r$  |
| 5536.....               | 10            | 10           | 10 $r$ |

It is very doubtful if the strontium lines, wave-lengths 5968 and 4032, are due to the metal. They should, if metallic lines, appear in both flame and arc spectra. The barium line  $\lambda$  6497 is probably due to the metal, as also is a line  $\lambda$  “4554 (?)” which Eder and Valenta attribute to the oxide of barium: it is present both in the oxyhydrogen and arc spectra.

The three lines in question are practically the only lines due to the metals in their Bunsen flame spectra: they are the strongest lines in the oxyhydrogen flame spectra, and they are reversed in the arc spectra. No other line has been observed which resembles them, so we conclude that they correspond to one another: that they are produced by similar motions of the molecules.

These lines are probably the only representatives of the principal series of these elements.

Rydberg also selects these three lines as corresponding to one another.

There are other lines in the oxyhydrogen spectra of these elements which must be considered. These present difficulties, and it is probable that it will be necessary to examine them under the “Zeeman effect,” before a final selection can be made. Some of the lines of barium which should correspond to those observed in calcium and strontium will probably be found in the red region of the spectrum. Ten lines have been observed on the less refrangible side of the line  $\lambda$  4227 in the spectrum of calcium; eleven have been observed in strontium on the less refrangible side of line  $\lambda$  4607, but none have

yet been observed corresponding to these in the spectrum of barium. On the more refrangible side of these three lines, two lines, corresponding to the solar lines H and K, wave-lengths 3968·8 and 3933·8, are found in calcium; two lines, wave lengths 4215·7 and 4077·9, in strontium, and seven lines in barium. The two calcium lines doubtless correspond to the two strontium lines, but it is very difficult to select the corresponding lines of barium. The two selected, and included on the diagrams, have wave-lengths 3890 and 3500, but they are the only lines about which serious doubt is held. We must not therefore attach much importance to them until the spectrum of barium has been fully examined and the selection confirmed.

Humphreys and Mohler\* found that the H and K lines of calcium were only shifted half as far as the 4226·9 line by changes of pressure.

Reese† has shown that under the Zeeman effect the 3933 line of calcium becomes a triplet and the 3968 line a quadruplet.

*Lithium and Sodium.*—There is no doubt but that the red lithium line corresponds to the yellow (D) lines of sodium. These lines are the strongest in the spectra, and there are no other lines of the principal series of these two elements nearer than wave-length 3303.

The two subordinate series may be easily arranged, according to the intensity of the lines: the lines of the diffuse series are much stronger than those of the sharp series.

*Potassium, Rubidium, and Cesium.*—Lines which, from their relative intensities in all spectra, appear to correspond to one another are:—

|                                      | Intensity. |              |          |
|--------------------------------------|------------|--------------|----------|
|                                      | Bunsen.    | Oxyhydrogen. | Arc.     |
| Potassium—<br>4047.....<br>4044..... | } 10 {     | 8<br>10      | 6r<br>8r |
| Rubidium—<br>4216.....<br>4202.....  |            | 8<br>10      | 6r<br>8r |
| Cesium—<br>4593.....<br>4555.....    | 9<br>10    | 6<br>10      | 6r<br>8r |

These are all given by the same value of  $m$  ( $= 2$ ) in Rydberg's formula for the principal series, and the other lines of the two series follow in order. The lines in the diffuse subordinate series were

\* 'Astrophys. Jour.,' vol. 3, 1896 p. 114.

† *Ibid.*, September, 1900.

selected in the same way, but our knowledge of these series is not as complete as our knowledge of the principal series. Kayser and Runge did not observe any lines in the sharp subordinate series of cæsium: no lines, therefore, of the sharp series appear on the diagrams.

*Copper, Silver, Gold.*—There are only two strong lines in the flame spectra of copper and silver, but some weak lines occur in the less refrangible region. The wave-lengths of the strong lines are:—Copper, 3274·1 and 3247·6; silver, 3380·8 and 3283·0.

A line with wave-length 2675 occurs in the oxyhydrogen flame spectrum of gold. It is much more refrangible, therefore, than the above lines of copper and silver, and is on this account much weaker; the same\* source of energy does not produce these more rapid motions with the same amplitude as the slower motions. This line and another of wave-length 2428 occur in the arc and spark spectra of gold: the two lines are easily reversed, and appear in all respects to correspond to the above doublets of copper and silver. Rydberg selected these six lines as the first members of the principal series of these metals. He gave the wave-lengths, on Ångström's scale, as:—

|                      | Copper. | Silver. | Gold.  |
|----------------------|---------|---------|--------|
| P <sub>2</sub> ..... | 3273·2  | 3382·3  | 2675·4 |
| P <sub>1</sub> ..... | 3246·9  | 3280·1  | 2427·5 |

There are also several remarkable† bands in the flame spectra of these three metals. The bands in the silver spectrum differ in character from those in the copper and gold spectra. Every band terminates in a sharp line on the more refrangible side. The lines forming the bands are sharper and more widely separated in the spectra of copper and gold than in the spectrum of silver.

*Magnesium, Zinc, Cadmium, Mercury.*—The flame spectra of the first three consist of lines and bands. The bands are very complicated in structure, and are degraded on the more refrangible side. Eder and Valenta‡ and Huff§ have described the production of a banded spark spectrum of mercury, which is similar in character to those of zinc and cadmium. No bands degraded in the same direction have been discovered in the spectra of other metals.

The following lines occur in the flame spectra of these metals:—

\* Hartley and Ramage, 'Trans. Roy. Dublin Soc.,' N.S., vol. 7, part xii, p. 341.

† Hartley and Ramage, *ibid.*

‡ 'Denkschr. K. Akad. Wien,' vol. 61, 1894.

§ 'Astrophys. Jour.,' Sept. 1900.



| Magnesium.                                             | Zinc.                                        | Cadmium.                                     | Mercury.   |
|--------------------------------------------------------|----------------------------------------------|----------------------------------------------|------------|
| 5184 }<br>5173 } triplet<br>5168 }<br>4571 }<br>2852 } | 4812 }<br>4722 } triplet<br>4680 }<br>3076 } | 5086 }<br>4800 } triplet<br>4678 }<br>3261 } | 547<br>435 |

Mercury appears to give only a continuous spectrum in the oxyhydrogen flame. Both zinc and cadmium give weak spectra, proving that the emissive power of their molecules in the oxyhydrogen flame is low compared with many other metals. Mitscherlich\* records two lines in the spectrum of cyanide of mercury, heated in the oxyhydrogen or oxycoal-gas flame, which correspond to two lines of the strongest triplet in the arc and spark spectra of mercury. The wavelengths of the lines of the triplet are 5460, 4359, and 4078. This triplet is given by the merest trace of mercury in a vacuum tube.

There is every reason for believing that the four triplets correspond to one another. The lines are all given by the same value of  $m$  in Rydberg's formula. The work of Preston,† of Lord Blythwood and Dr. Marchant,‡ and of Reese§ on the Zeeman effect give additional support to this view.

| Observer.                                                              | Magnesium, zinc, and cadmium.          |                                     | Mercury.                |                                          | Mercury.                                          |
|------------------------------------------------------------------------|----------------------------------------|-------------------------------------|-------------------------|------------------------------------------|---------------------------------------------------|
|                                                                        | Preston.                               |                                     | Blythwood and Marchant. |                                          | Reese.                                            |
| Strength of magnetic field.<br>C.G.S. units.                           | 20,000                                 | 40,000                              | 6,000                   | 24,000                                   | 24,500                                            |
| Least refrangible line<br>Middle line . . . .<br>Most refrangible line | Nebulous triplet<br>Quartet<br>Triplet | Triple triplet<br>Sextet<br>Triplet | Triplet<br>Quartet<br>— | Doublet, triplet, doublet<br>Sextet<br>— | Triplet, "probably more."<br>Triplet.<br>Triplet. |

There remain the isolated lines: two of magnesium and one each of zinc and cadmium.

\* 'Phil. Mag.,' Sept. 1864, plate.

† 'Trans. Roy. Dublin Soc.,' vol. 7, series ii, No. 2.

‡ 'Phil. Mag.,' vol. 49, p. 384, 1900.

§ 'Astrophys. Jour.,' Sept. 1900, p. 120.

|| Gray has now resolved this into nine lines, 'Brit. Assoc.,' 1901.

The four lines occur in the arc spectra of their respective elements : the zinc line is in Kayser's and Runge's tables, marked 8r ; the magnesium line 4574 is marked 4, the remaining two 10r. These characters indicate that the magnesium line  $\lambda$  2852 corresponds to the lines of zinc and cadmium. The magnesium line  $\lambda$  2852 has not been examined under the Zeeman effect, but the zinc line breaks up into a "very sharp triplet" and the cadmium line into a "triplet" (Reese). The magnesium line is given when a very small quantity of the element is heated in the oxyhydrogen flame, or by a very short exposure ; it furnishes, in fact, a delicate test for the element. All this evidence indicates that the line  $\lambda$  2852 corresponds to the zinc and cadmium lines.

Rydberg says (p. 106) of the magnesium line  $\lambda$  2852 : "It is probable. . . . (it) corresponds to the strongest lines in the spectra of the elements :"—Calcium 4226, strontium 4607, and barium 5534. The evidence furnished by the oxyhydrogen flame spectra is against this conclusion, for it shows no similarity between the spectrum of magnesium and those of the calcium group. The bands in the flame spectra of the calcium group are degraded on the less refrangible side, and they are quite different in character from those of the zinc group.

Rydberg says (p. 114) that the lines of zinc 3075.6 and cadmium 3260.12 "correspond perfectly." He does not refer to a corresponding line in the spectrum of mercury. There is one, doubtless, and its discovery will be of considerable interest.

Ames\* selected the following lines from the arc spectra. Magnesium 2852.2, zinc 2138.3, and cadmium 2288.1. These lines of zinc and cadmium have not been observed in the oxyhydrogen spectra. Even if present they must, on account of their high refrangibility, be very weak. The zinc line  $\lambda$  3076, lies, in the flame spectrum, among the lines in the strongest water vapour group, and it was photographed for the first time, in a special search for it, in May, 1900.

*The Aluminium Group.*—All the lines found in the flame spectra of the metals of this group are used in the investigation. The selection of the corresponding lines presents no difficulty, as the corresponding lines are clearly indicated by the relative intensity of the lines, and by the fact that the less refrangible member of one series of doublets is itself double. Five lines have been observed in the flame spectrum of gallium, but this spectrum has not been fully examined. The wave-lengths of the other five lines were determined on two photographs of the spark spectrum of gallium which Professor Liveing very kindly lent me.

Exner and Haschek have measured some lines in the spark spectrum of gallium.†

\* *Loc. cit.*

† 'Akad. Wiss. Wien, Sitzb., 108, p. 1120, 1899.

Reese has shown that the 3944 line of aluminium yields, under the Zeeman effect, a quadruplet and the 3961 line a triplet.

If we confine our attention to the lines of the flame spectra of the metals the diagrams are comparatively simple. The work may be extended, however, by including the more refrangible lines in the arc and spark spectra of several metals. Rydberg's formula, and the formula of Kayser and Runge, will assist greatly in this extension of the work.

The study of the effect of a magnetic field on the source of light (the "Zeeman Effect") will be of great importance in confirming the selection of a few of the lines included in the present paper, and in the prosecution of the investigation in the future.

The more refrangible lines are always feeble and nebulous compared with the less refrangible members of the series, and it is more difficult to obtain accurate measurements of these weaker lines. The principal series of lithium furnishes us with a typical example of this difficulty. The lines were measured in the arc spectrum by Kayser and Runge.

| Wave-lengths. | Limit of error. | Intensity.<br>10 = maximum. |
|---------------|-----------------|-----------------------------|
| 6708·2        | 0·2             | 10                          |
| 3232·77       | 0·03            | 8                           |
| 2741·39       | 0·03            | 6                           |
| 2562·60       | 0·03            | 4                           |
| 2475·13       | 0·1             | 4                           |
| 2425·55       | 0·1             | 2                           |
| 2394·54       | 0·2             | 1                           |

If we except the line in the extreme red, the accuracy of the determination of the wave-lengths diminishes with the intensity and refrangibility of the line.

#### *Discussion of the Diagrams (Plates 1 and 2).*

The diagrams were first drawn with the atomic masses as ordinates, and the lines connecting corresponding lines were nearly all curved. Dr. J. H. Vincent, of this college, suggested to me, in February, 1900, that different functions of the atomic masses should be used as ordinates, so that as many of these curved lines as possible should be converted into straight lines. It was found immediately that, by taking the squares of the atomic masses, the line joining the strongest lines of calcium, strontium, and barium—wave-lengths 4227, 4608, and 5536 respectively—was very nearly straight.

Diagrams have since been drawn to this scale, both in oscillation frequencies and in wave-lengths, of all the lines enumerated above.

## List of the Corresponding Lines included in the Diagrams.

| <i>m.</i> | Wave-length. | Intensities. |        |                 |        | <i>m.</i> | Wave-length.                    | Intensities. |        |                 |        |
|-----------|--------------|--------------|--------|-----------------|--------|-----------|---------------------------------|--------------|--------|-----------------|--------|
|           |              | Bunsen.      | Oxy-H. | Arc.            | Spark. |           |                                 | Bunsen.      | Oxy-H. | Arc.            | Spark. |
|           | Lithium.     |              |        |                 |        |           | Potassium—<br><i>continued.</i> |              |        |                 |        |
| 1         | 6708·2       | 10           | 10     | 10 <sub>r</sub> | 10     | 6         | 3034·94                         | —            | —      | 4 <sub>r</sub>  | 4      |
| 2         | 3232·82      | 4            | 4      | 8 <sub>r</sub>  |        | 7         | 2992·33                         | —            | —      | 2 <sub>r</sub>  |        |
| 3         | 2741·43      | —            | 1      | 6 <sub>r</sub>  |        | 8         | 2963·36                         | —            | —      | 1 <sub>r</sub>  |        |
| 4         | 2562·60      | —            | —      | 4 <sub>r</sub>  |        | 9         | 2942·8                          | —            | —      | 1 <sub>r</sub>  |        |
| 5         | 2475·13      | —            | —      | 4 <sub>r</sub>  |        |           |                                 |              |        |                 |        |
| 6         | 2425·55      | —            | —      | 2 <sub>r</sub>  |        |           |                                 |              |        |                 |        |
| 7         | 2394·54      | —            | —      | 1 <sub>r</sub>  |        |           |                                 |              |        |                 |        |
| 8         | 2373·9       | —            | —      | < 1             |        |           |                                 |              |        |                 |        |
| 9         | 2359·4       | —            | —      | < 1             |        |           |                                 |              |        |                 |        |
|           | Sodium.      |              |        |                 |        |           | Rubidium.                       |              |        |                 |        |
| 1         | 5896·16      | 10           | 10     | 10 <sub>r</sub> | 10     | 1         | 7950·46                         | 4            | 9      | 10 <sub>r</sub> |        |
| 1         | 5890·19      | 10           | 10     | 10 <sub>r</sub> | 10     | 1         | 7805·98                         | 8            | 10     | 10 <sub>r</sub> |        |
| 2         | 3303·07      | 8            | 3      | 8 <sub>r</sub>  | 10     | 2         | 4215·68                         | 9            | 9      | 6 <sub>r</sub>  |        |
| 2         | 2·47         | —            | 4      | 8 <sub>r</sub>  | 10     | 2         | 02·04                           | 10           | 10     | 8 <sub>r</sub>  |        |
| 3         | 2853·02      | 2            | 2      | 6 <sub>r</sub>  | 10     | 3         | 3591·86                         | —            | 3      | 4 <sub>r</sub>  |        |
| 4         | 2680·70      | —            | 1      | 4 <sub>r</sub>  | 8      | 3         | 87·27                           | —            | 4      | 6 <sub>r</sub>  |        |
| 5         | 2593·98      | —            | —      | 2 <sub>r</sub>  | 3      | 4         | 3350·98                         | —            | 1      | 2 <sub>r</sub>  |        |
| 6         | 2543·85      | —            | —      | 1 <sub>r</sub>  | 1      | 4         | 48·84                           | —            | 2      | 4 <sub>r</sub>  |        |
| 7         | 2512·23      | —            | —      | 1 <sub>r</sub>  | 1      | 5         | 3229·26                         | —            | 1      |                 |        |
|           | Potassium.   |              |        |                 |        | 5         | 8·18                            | —            | 1      |                 |        |
|           |              |              |        |                 |        |           | Cæsium.                         |              |        |                 |        |
| 1         | 7699·3       | 10           | 10     | 10 <sub>r</sub> |        | 1         | 8949·92                         | —            | —      | 9               |        |
| 1         | 7655·6       | 10           | 10     | 10 <sub>r</sub> |        | 1         | 8527·72                         | —            | —      | 10              |        |
| 2         | 4047·39      | 10           | 9      | 6 <sub>r</sub>  |        | 2         | 4593·30                         | 9            | 8      | 6 <sub>r</sub>  |        |
| 2         | 4044·33      | 10           | 10     | 8 <sub>r</sub>  | 10     | 2         | 55·46                           | 10           | 10     | 8 <sub>r</sub>  |        |
| 3         | 3447·56      | 4            | 3      | 6 <sub>r</sub>  | 10     | 3         | 3888·75                         | —            | 2      | 4 <sub>r</sub>  |        |
| 3         | 6·55         | 4            | 4      | 8 <sub>r</sub>  | 10     | 3         | 76·31                           | —            | 4      | 6 <sub>r</sub>  |        |
| 4         | 3217·76      | 1            | 1      | 4 <sub>r</sub>  | 2      | 4         | 3617·49                         | —            | < 1    | 2 <sub>r</sub>  |        |
| 4         | 7·27         | —            | 2      | 6 <sub>r</sub>  | 1      | 4         | 1·70                            | —            | 2      | 4 <sub>r</sub>  |        |
| 5         | 3102·37      | —            | —      | 2 <sub>r</sub>  | 1      | 5         | 3447·25                         | —            | 1      |                 |        |
| 5         | 2·15         | —            | —      | 4 <sub>r</sub>  | 1      | 6         | 3398·40                         | —            | 1      |                 |        |
|           |              |              |        |                 |        | 7         | 48·72 ?                         | —            | < 1    |                 |        |
|           |              |              |        |                 |        | 8         | 14·0                            | —            | < 1    |                 |        |
|           |              |              |        |                 |        | 9         | 3287·0                          | —            | < 1    |                 |        |

| Wave-length. | Intensities.  |        |                 |        | Wave-length. | Intensities.  |        |                 |        |
|--------------|---------------|--------|-----------------|--------|--------------|---------------|--------|-----------------|--------|
|              | Bunsen flame. | Oxy-H. | Arc.            | Spark. |              | Bunsen flame. | Oxy-H. | Arc.            | Spark. |
| Copper.      |               |        |                 |        | Gold.        |               |        |                 |        |
| 3274·11      | —             | 9      | 10 <sub>r</sub> | 8      | 2676·05      | —             | 3      | 10 <sub>r</sub> | 8      |
| 3247·68      | —             | 10     | 10 <sub>r</sub> | 10     | 2423·10      | —             | —      | 10 <sub>r</sub> | 10     |
| Silver.      |               |        |                 |        |              |               |        |                 |        |
| 3383·06      | —             | 10     | 10 <sub>r</sub> | 10     |              |               |        |                 |        |
| 3280·84      | —             | 10     | 10 <sub>r</sub> | 10     |              |               |        |                 |        |
| Calcium.     |               |        |                 |        | Barium.      |               |        |                 |        |
| 4226·91      | 10            | 10     | 10 <sub>r</sub> | 12     | 5535·69      | 10            | 10     | 10 <sub>r</sub> | 10     |
| 3968·83      | —             | 3      | 10 <sub>r</sub> | 10     | 3889·45      | —             | 2      | 4               |        |
| 3933·83      | —             | 4      | 10 <sub>r</sub> | 10     | 3501·25      | —             | 3      | 10              | 10     |
| Strontium.   |               |        |                 |        |              |               |        |                 |        |
| 4607·45      | 10            | 10     | 10              | 10     |              |               |        |                 |        |
| 4215·66      | —             | 4      | 10 <sub>r</sub> | 10     |              |               |        |                 |        |
| 4077·88      | —             | 3      | 10              | 10     |              |               |        |                 |        |
| Magnesium.   |               |        |                 |        | Cadmium.     |               |        |                 |        |
| 5138·84      | —             | 10     | 10 <sub>r</sub> | 10     | 5086·06      | —             | 10     | 10 <sub>r</sub> | 10     |
| 5172·87      | —             | 9      | 10 <sub>r</sub> | 9      | 4800·09      | —             | 9      | 10 <sub>r</sub> | 10     |
| 5167·55      | —             | 8      | 8 <sub>r</sub>  | 8      | 4678·37      | —             | 8      | 10 <sub>r</sub> | 10     |
| 2852·21      | —             | 10     | 10 <sub>r</sub> | 10     | 3261·18      | —             | 10     | 10 <sub>r</sub> | 8      |
| Zinc.        |               |        |                 |        | Mercury.     |               |        |                 |        |
| 4801·71      | —             | 10     | 10 <sub>r</sub> | 10     | 5790·49      | —             | —      | 10 <sub>r</sub> | 10     |
| 4722·26      | —             | 9      | 10 <sub>r</sub> | 10     | 5769·45      | —             | —      | 10 <sub>r</sub> | 10     |
| 4680·38      | —             | 8      | 10 <sub>r</sub> | 10     | 5460·97      | —             | —      | 10 <sub>r</sub> | 10     |
| 3076·02      | —             | 10     | 8 <sub>r</sub>  | 8      |              |               |        |                 |        |
| Aluminium.   |               |        |                 |        | Indium.      |               |        |                 |        |
| 3961·68 }    | —             | 10     | 10 <sub>r</sub> | 9      | 4511·44 }    | 10            | 10     | 10 <sub>r</sub> | 10     |
| 3944·16 }    | —             | 10     | 10 <sub>r</sub> | 9      | 4101·87 }    | 10            | 9      | 8 <sub>r</sub>  | 9      |
| 3092·95 }    | —             | 3      | 6 <sub>r</sub>  | 9      | 3258·71 }    | —             | 3      | 6 <sub>r</sub>  | 9      |
| 3092·84 }    | —             | —      | 10 <sub>r</sub> | 9      | 6·22 }       | —             | 4      | 10 <sub>r</sub> | 10     |
| 3082·27 }    | —             | 3      | 10 <sub>r</sub> | 9      | 3039·46 }    | —             | 4      | 10 <sub>r</sub> | 10     |
| 2660·49 }    | —             | —      | 10 <sub>r</sub> | 5      | 2932·71 }    | —             | 2      | 6 <sub>r</sub>  | 7      |
| 2652·56 }    | —             | —      | 10 <sub>r</sub> | 5      | 2753·77 }    | —             | 1      | 6 <sub>r</sub>  | 5      |
| 2575·49 }    | —             | —      | 6 <sub>r</sub>  | 7      | 2714·05 }    | —             | >1     | 6 <sub>r</sub>  | 3      |
| 2575·20 }    | —             | —      | 10 <sub>r</sub> | 7      | 10·38 }      | —             | —      | 10 <sub>r</sub> | 7      |
| 2568·08 }    | —             | —      | 10 <sub>r</sub> | 7      | 2560·25 }    | —             | —      | 8 <sub>r</sub>  | 7      |

| Wave-length. | Intensities.  |        |      |        | Wave-length. | Intensities.  |        |      |        |
|--------------|---------------|--------|------|--------|--------------|---------------|--------|------|--------|
|              | Bunsen flame. | Oxy-H. | Arc. | Spark. |              | Bunsen flame. | Oxy-H. | Arc. | Spark. |
| Gallium.     |               |        |      |        | Thallium.    |               |        |      |        |
| 4172·21 }    | —             | 10     | 10   | 10     | 5350·65 }    | 10            | 10     | 10r  | 10     |
| 4033·12 }    | —             | 9      | 9    | 9      | 3775·87 }    | —             | 10     | 10r  | 10     |
| 2943 }       | —             | 2      | —    | 3      | 3529·58 }    | —             | 3      | 8r   | 10     |
| 2 }          | —             | 3      | —    | 4      | 19·39 }      | —             | 4      | 10r  | 10     |
| 2873 }       | —             | 3      | —    | 4      | 2767·97 }    | —             | 3r     | 10r  | 10     |
| 2780 }       | —             | —      | —    | 3      | 3229·88 }    | —             | 3      | 10r  | 8      |
| 2718 }       | —             | —      | —    | 2      | 2580·23 }    | —             | —      | 8r   | 8      |
| 2496 } broad | —             | —      | —    | 2      | 2921·63 }    | —             | 1      | 6r   | 8      |
| 2447 }       | —             | —      | —    | 1      | 18·43 }      | —             | —      | i r  | 10     |
|              |               |        |      |        | 2379·66 }    | —             | —      | s    | 8      |

Diagrams have been drawn with other functions of the atomic mass, but they have not given results of any great value.

The diagrams reproduced in Plates 1 and 2 were drawn from the oscillation frequencies of the lines and (1) the atomic masses, (2) the squares of the atomic masses. The symbols indicate the positions of the lines in the spectra.

The following facts have been observed in the study of the diagrams :—

- (1.) The metals considered may be classified into groups, according to their spectra. The fact is not new, but the diagrams make its truth most obvious.
- (2.) The connecting lines between the members of the groups are not continuous : there are certain breaks in them. There is a break in the group of the metals of the alkalis between sodium and potassium. Another break occurs between the triplet of magnesium and those of zinc, cadmium, and mercury.

There are members of two subordinate series in the spectra of the aluminium group—the sharp and the nebulous series. The break between aluminium and the other metals is very marked in the diffuse series, while there is only a slight irregularity in the lines connecting the sharp series. This fact will be referred to again when considering the physical properties of the metals.

- (3.) The cause of the displacement of corresponding lines in some strictly homologous spectra is intimately connected with the change in the atomic mass. The lines are moved towards the less refrangible end of the spectrum with an increase in the atomic mass. The shift of the lines due to this cause is most

evident in the lines of the metals of the alkalis, particularly of potassium, rubidium, and cæsium, and in the strongest lines of calcium, strontium, and barium.

In Plate 1 the lines joining the diffuse subordinate series of the potassium group approach to straight lines in the more refrangible members of the series, and the lines joining the principal series are nearly parabolic. The latter are nearly straight in the more refrangible members in Plate 2. The shift of the subordinate lines is approximately proportional to the atomic mass, and the shift of the principal lines to the square of the atomic mass.

The fundamental lines of calcium, strontium, and barium are given by the equation  $n = 24170 - 0.3232 W^2$ , in which  $n = 10^8 \lambda^{-1}$  and  $W$  = atomic mass. The differences from the observed values are—calcium 0, strontium -7, and barium +9.

The atomic mass is not the only cause which determines the shift of the lines. There are, doubtless, other causes at work, and it is probably in these we must seek the explanation of the abnormal shifts which produce the breaks in the connecting lines referred to above. In passing from group to group, for instance, an increase in the valency with but slight increase in the atomic mass results in the whole of a series being displaced to a considerable extent. The following figures have been taken to illustrate this point from Rydberg's "*La Distribution des Raies Spectrales*," read to the Congrès International de Physique de 1900:—

| Element.         | Atomic Mass. | Difference in Atomic Mass. | Valency. | Limit of Series.         | Difference in limit of series. |
|------------------|--------------|----------------------------|----------|--------------------------|--------------------------------|
|                  |              |                            |          | Oscillation Frequencies. |                                |
| Sodium . . . . . | 23.06        | 1.32<br>2.70               | I        | 24470                    | 15285<br>8401                  |
| Magnesium ..     | 24.38        |                            | II       | 39755                    |                                |
| Aluminium ..     | 27.08        |                            | III      | 48156                    |                                |
| Silver . . . . . | 107.94       | 4.14<br>1.62               | I        | 30648                    | 10069<br>3731                  |
| Cadmium ....     | 112.08       |                            | II       | 40717                    |                                |
| Indium . . . . . | 113.7        |                            | III      | 44448                    |                                |

The figures in the fifth and sixth columns refer to the subordinate series of lines.

Changes of valency therefore produce much greater displacements of the spectral lines than changes in the atomic masses.

Another cause is doubtless at work in the elements—copper, silver, and gold. The connecting lines here take a remarkable form, and this form is seen also in the lines selected as corresponding to the H and K solar lines of calcium in the spectra of calcium, strontium, and barium.

Many of the chemical and physical properties of these elements have been considered, and the only common property yet discovered is connected with the atomic volume.

|        | Atomic<br>volume. |           | Atomic<br>volume. |
|--------|-------------------|-----------|-------------------|
| Copper | 7.2               | Calcium   | 25                |
| Silver | 10                | Strontium | 35                |
| Gold   | 10                | Barium    | 36                |

The atomic volumes of the two elements of higher atomic weights in each group are almost identical.

If it should prove that the two lines of barium do not correspond to the strontium and calcium lines, we may find that the remarkable curves joining the lines of copper, silver, and gold are connected with the valency of these metals. The curve of melting points takes a peculiar form also in these three metals.

(4.) *Intersection of the Lines connecting Homologous Doublets and Triplets.*

Rydberg\* denoted by  $v$  the difference in oscillation frequencies: (1) between the members of doublets; (2) between the two more widely separated lines in triplets. He made the following observations:—1st. “The value of  $v$  increases in special families with increase of atomic weight.” 2nd. “The constant  $v$  is, without doubt, a very complicated function of the atomic weight.”

These observations were made entirely on the subordinate series of lines, and he found that the values of  $10^{3v}/P^2$  (where  $P$  = the atomic weight) were a periodic function of the atomic weight. He has given a more complete diagram of this in his paper to the Congrès de Physique, Paris, 1900.

Rydberg's first observation is very clearly shown on my diagrams. We learn further from them that in special families the value of  $v$  is largely dependent upon the atomic mass, and that the function is closely related to the square of the atomic mass. Plate 2, drawn from these squares, shows that the lines which connect corresponding members of homologous doublets and triplets approach one another as the atomic mass decreases and *intersect on the line of zero atomic mass*. This is true in every case studied, both in the subordinate series, with constant differences of oscillation frequency, and in the principal series of potassium, rubidium, and cesium, and in isolated doublets.

It is evident that the points of intersection of these connecting lines cannot be absolutely determined, and a large personal element may be introduced in some cases. This personal element cannot, however, be large in the potassium and aluminium groups, where the

\* ‘Kongl. Svenska Vetensk. Akad. Handl.,’ 1890, vol. 23, No. 11.



ordinates representing the elements with the lowest atomic masses are very close to the ordinate representing zero atomic mass.

It may be remarked that, even if it could be shown positively that the lines do not intersect on the line of zero atomic mass, they must intersect in points very near to it. Any disturbing influence must be so small that the statement may be accepted as a broad fundamental fact, as far as the elements under consideration are concerned.

- (5.) The form of some of the connecting lines indicates that no element will be found of greater atomic mass than the greatest represented. This is seen most strikingly in the connecting lines of copper, silver, and gold.

### *The Homologous Series of Spectral Lines.*

Rydberg has classed together as "Lines of Type I," the series found in the spectra of hydrogen, helium, lithium, oxygen, sodium, magnesium, aluminium, sulphur, potassium, calcium, copper, zinc, selenium, rubidium, strontium, silver, cadmium, indium, caesium, mercury, and thallium. To these may be added gallium.

The series have been further divided into three kinds: the principal series and two subordinate series.

Only the metals of the alkalis yield principal series, and this part of the paper will deal almost wholly with these principal series. It is probable that the strongest lines of the calcium group, and the very strong doublets in the spectra of the copper group, belong to the principal series.

### *The Formulæ which have been Applied to Harmonic Series.*

Balmer was the first to give a formula for the harmonic series of lines in the spectrum of hydrogen.\* His formula is:—

$$\lambda = h \frac{m^2}{m^2 - 4}.$$

Rydberg gave† a general formula, applicable to all these series:  $n = n_\infty - \frac{N_0}{(m + \mu)^2}$ , where  $n = 10^8 \lambda^{-1}$ ;  $n_\infty$  and  $\mu$  are constants for each series.  $N_0$  is a constant common to all series, and  $m = 1, 2, 3 \dots$

Kayser and Runge have given the formula—

$$10^8 \lambda^{-1} = A - Bn^{-2} - Cn^{-4},$$

where  $n = 3, 4, 5 \dots$  and A, B, C are constants in each series. The constants B and C apply generally to the subordinate series of monad

\* 'Wied. Ann.,' vol. 25, pp. 80–87, 1885.

† *Loc. cit.*

and triad metals. The constant  $B$  is approximately equal to Rydberg's constant  $N_0$ , but a different value is used in different series.

Modifications of these formulæ have been proposed by Ames,\* by Balmer,† and by Thiele.‡

The formula of Rydberg is of wide application, its form is simple, and the values of the constants are easily calculated. It has every appearance of being a more natural formula than that of Kayser and Runge. This is an important consideration, for there is doubtless some common cause acting to produce series of this type. The view has been expressed by Rydberg that: "The equation of Kayser and Runge is a formula of interpolation, which has no other object than to represent with the greatest accuracy possible the given observations." For these reasons we shall proceed to discuss it in detail, with special regard to its application to the principal series of lines.

*The Constant  $N_0$ .*—This constant was calculated from the lines in the hydrogen series— $N_0 = 4.10^8/h$ . Rydberg has given two values: (1) In 1890, the value 109721.6; and (2) in 1900, 109675.00.

Using the figures given by Ames for the hydrogen lines,§ we have obtained the number 109706. Dyson|| used the number 109705, and we have calculated the same number from the strongest hydrogen lines in Rowland's 'Solar Spectrum Wave-lengths.' By reducing the wave-lengths of Rowland to their corresponding values in a vacuum, we calculated the value of  $N_0$  as 109674. It would appear that Rydberg's later value must have been obtained in this manner.

In my earlier work, the value of  $N_0$  was taken as 109706, and in the later as 109675. The oscillation frequencies were in like manner reduced to their value in a vacuum.

The lines in the plates which accompany this paper are those given by the lower values of  $m$  in Rydberg's formula, and it is in these, especially in the strongest lines, where  $m = 1$ , that the formula, as used by its author, gives the greatest differences from the observed numbers. Rydberg only claims that his formula is approximately true, but the fact that it is of such general application is strong evidence for thinking it may be made more accurate. Certain facts revealed by a study of the diagrams, referred to above, and of the calculations made by Rydberg's method, indicate a modification of the formula, which will give much greater accuracy.

*The Principal Series of the Metals of the Alkalies.*—Each metal, except lithium, gives two principal series, the corresponding members of

\* 'Wied. Ann.,' vol. 25, pp. 80–87, 1885.

† 'Verhandl. d. Naturf. Ges. in Basel,' vol. 11, pp. 448–462.

‡ 'Astrophys. Jour.,' vol. 6, p. 65.

§ 'Phil. Mag.,' vol. 30, 1890, p. 33.

|| 'Roy. Soc. Proc.,' vol. 68, p. 33, 1901.

which form doublets. The differences in oscillation frequencies between these doublets are not constant, as in the doublets of the subordinate series; they diminish as the refrangibility increases.

The lines corresponding to the following values of  $m$  were known when this part of the work was done:

Lithium 1—9, sodium, 1—7; and potassium 1—9, rubidium 1—4, cæsium 2—7.

The differences between the observed and calculated numbers, when Rydberg's method is used, are given in the following series of potassium. The lines  $m = 2$ —7 were used to calculate the constants; the line  $m = 1$  was omitted, so that the constants might be compared with the corresponding constants of rubidium and cæsium.

| $m$ . | Calculated<br>number.<br>$10^8 \lambda^{-1}$ . | Observed<br>number.<br>$10^8 \lambda^{-1}$ . | Differences. |
|-------|------------------------------------------------|----------------------------------------------|--------------|
| 1     | 13584                                          | 13042                                        | + 542        |
| 2     | 24719                                          | 24719                                        | 0            |
| 3     | 28991                                          | 29006                                        | - 15         |
| 4     | 31069                                          | 31073                                        | - 4          |
| 5     | 32233                                          | 32226                                        | + 7          |
| 6     | 32950                                          | 32940                                        | + 10         |
| 7     | 33424                                          | 33409                                        | + 15         |

Similar results were obtained with all the principal series: the differences increased slightly with the atomic mass.

Several lines have been measured in the oxyhydrogen flame spectra of the elements—potassium, rubidium, and cæsium. The results are, in some cases at least, more accurate than those of Kayser and Runge: the differences between the measurements of the same lines on different plates are smaller than the limits of error given by them. Some of the lines have not been measured before.

The oscillation frequencies, reduced to their values in a vacuum, were used in the following calculations, and the value of  $N_0$  (109675) corresponding to this reduction was also used.

The chief points to be noted in the calculations are as follows:—

The value of the limit of the series diminishes as the refrangibility of the line, from which its position is calculated, increases, until an almost constant value is reached in the lines corresponding to values of  $m$  greater than 4. These lowest and almost constant values are, therefore, nearest to the true limits of the series.

The spectra indicate that the value of  $n_\infty$  must be the same for both series:—

| <i>m.</i> | Differences in Oscillation Frequencies, $P_1 - P_2$ . |            |           |         |
|-----------|-------------------------------------------------------|------------|-----------|---------|
|           | Sodium.                                               | Potassium. | Rubidium. | Cæsium. |
| 1         | 17                                                    | 57         | 225       | 564     |
| 2         | 5                                                     | 19         | 77        | 181     |
| 3         | —                                                     | 8          | 35        | 80      |
| 4         | —                                                     | 5          | 20        | 40      |
| 5         | —                                                     | 2          |           |         |
| 6         |                                                       |            |           |         |
| 7         |                                                       |            |           |         |

These figures show that the two series merge into one in both sodium and potassium, and that in rubidium and cæsium they are rapidly approaching each other. When  $m = \infty$ , therefore, they must have the same value, and  $n_\infty$ , corresponding to this, must be common to the two series.

When we take this view it is pretty evident that the value of  $\mu$  must vary throughout the series. It diminishes as the refrangibility of the line decreases, and, at the same time, the intensity of the line increases.

The differences between the values of  $\mu$  for the corresponding lines of the two series of each element are very nearly constant. The figures are as follows:—

| <i>m.</i> | Differences between values of $\mu$ . Series $P_1$ —Series $P_2$ . |           |          |
|-----------|--------------------------------------------------------------------|-----------|----------|
|           | Potassium.                                                         | Rubidium. | Cæsium.  |
| 1         | 0·0029                                                             | 0·0122 ?  | 0·0331 ? |
| 2         | 0·0030                                                             | 0·0129    | 0·0321   |
| 3         | 0·0029                                                             | 0·0130    | 0·0320   |
| 4         | 0·0033                                                             | 0·0132    | 0·0317   |
| 5         | 0·0022                                                             |           |          |

The mean values of these are proportional to the squares of the atomic masses, and are given by the term  $18W^2 \times 10^{-7}$ .

The diagrams prove that there is a very close relation between the spectra of the three elements under consideration and the atomic masses. Rydberg's equation has, therefore, been modified in accordance with the above work, and an empirical formula has been obtained, which contains only one variable,  $W$  the atomic mass. One equation, the following, gives the second principal series of all three metals with considerable accuracy:—

$$n = 35349 - 0.2233W^2 - \frac{109675}{\{m+1+(2-3^{-m})(0.1143+0.000625W)\}^2}$$

The factor  $(2-3^{-m})$  corrects for the variations in the fractional parts of  $\mu$ , referred to above.

The first principal series are obtained by adding to  $m+1$  in the denominator the term  $18W^2 \times 10^{-7}$ .

[A closer approximation is given when, in Rydberg's general formula,

$$n = n_{\infty} - \frac{N}{(m+\mu)^2}$$

we substitute

$$n_{\infty} = 35349 - 0.2233W^2; \quad N_0 = 109675,$$

and

$$\mu = \{1.19126 + 0.00103W + (0.04377 + 13W^2 \times 10^{-7})(1 - 3^{1-m})\}.$$

These values give the second principal series of potassium, rubidium, and caesium. To obtain the first principal series, increase the value of  $\mu$  by  $182W^2 \times 10^{-8}$ . The value of  $n_{\infty}$ , which the above gives for rubidium, is 27.5 units too great.

The wave-numbers ( $10^8\lambda^{-1}$ ), calculated from this amended formula, are compared with the observed values in the following tables:—

#### Potassium.

| <i>m</i> . | Second Series. |             |               | First Series. |             |               |
|------------|----------------|-------------|---------------|---------------|-------------|---------------|
|            | Observed.      | Calculated. | Differ-ences. | Observed.     | Calculated. | Differ-ences. |
| 1          | *12984.5       | 12983.1     | -1.4          | *13041.5      | 13038.0     | -3.5          |
|            | †12980.0       |             | +3.1          | †13036.6      |             | +1.4          |
| 2          | 24700.3        | 24700.5     | +0.2          | 24719.0       | 24718.1     | -0.9          |
| 3          | 28997.8        | 27998.4     | +0.6          | 29006.3       | 29006.2     | -0.1          |
| 4          | 31068.0        | 31066.8     | -1.2          | 31072.7       | 31070.9     | -1.8          |
| 5          | *32224.0       | 32223.6     | -0.4          | *32225.8      | 32226.0     | +0.2          |
| 6          |                |             |               | *32939.5      | 32937.9     | -1.6          |
| 7          |                |             |               | *33408.5      | 33407.1     | -1.4          |

\* Kayser and Runge.

† Lehmann, 'Ann. d. Physik,' vol. 5, p. 633, 1901. Unmarked lines observed by the Author (Flame Spectra).

| <i>m.</i> | Second Series.       |             |                            | First Series.        |             |                            |
|-----------|----------------------|-------------|----------------------------|----------------------|-------------|----------------------------|
|           | Observed.            | Calculated. | Differ-<br>ences<br>-27·5. | Observed.            | Calculated. | Differ-<br>ences<br>-27·5. |
| 1         | *12575·0<br>†12574·3 | 12608·2     | +5·7<br>+6·4               | *12799·7<br>†12806·9 | 12851·9     | +24·7<br>+17·5             |
| 2         | 23714·4              | 23738·6     | -3·3                       | 23791·4              | 23818·1     | -0·8                       |
| 3         | 27832·8              | 27861·5     | +1·2                       | 27868·4              | 27897·3     | +1·4                       |
| 4         | 29833·5              | 29860·6     | -0·4                       | 29852·6              | 29879·8     | -0·3                       |
| 5         | 30958                | 30984·9     | -0·6                       | 30968·4              | 30996·2     | +0·3                       |

Caesium.

| <i>m.</i> | Second Series. |             |                   | First Series. |             |                   |
|-----------|----------------|-------------|-------------------|---------------|-------------|-------------------|
|           | Observed.      | Calculated. | Differ-<br>ences. | Observed.     | Calculated. | Differ-<br>ences. |
| 1         | †11169·8       | 11170·9     | +1·1              | †11723·0      | 11718·4     | -4·6              |
| 2         | 21764·8        | 21763·1     | -1·7              | 21945·6       | 21944·3     | -1·3              |
| 3         | 25707·9        | 25707·7     | -0·2              | 25790·4       | 25790·3     | -0·1              |
| 4         | 27635·7        | 27633·4     | -2·3              | 27680·0       | 27677·9     | -2·1              |
| 5         | —              | —           | —                 | 28750·3       | 28749·3     | -1·0              |
| 6         | —              | —           | —                 | 29417·3       | 29416·7     | -0·6              |

This formula, though empirical, involves only seven adjustable constants; in these tables it represents, in the two series, thirty-two lines. It thus affords striking evidence for the fundamental identity of type of the spectra of the three metals to which it applies, and indicates that their differences depend on the atomic mass alone. This evidence is further strengthened when it is remembered that, being only an approximation to an unknown formula, it will naturally come nearer it for large values of *m* than for small ones. Additional evidence supporting these views is given above by the observations upon the subordinate series of these three metals, in which the differences depend directly on the atomic mass, and upon the fundamental spectra of calcium, strontium, and barium, in which the differences depend on the square of the atomic mass.—*Added January 27, 1902.*]

Rydberg's formula and method give better results for the series

\* Kayser and Runge.

† Lehmann, 'Ann. d. Physik,' vol. 5, p. 633, 1901. Unmarked lines observed by the Author (Flame Spectra).

of lines belonging to elements of low atomic mass, such as hydrogen, helium, and lithium, than for the others. The differences between the observed and calculated numbers increase in magnitude with the atomic mass.

The suggestion to take the highest value of  $\mu$ , that derived from the more refrangible lines, as the starting point, appears to be perfectly fair. When this is done, we observe that the differences between the numbers calculated with this  $\mu$  as a constant for the series and the observed numbers increase with the intensity of the lines. There is, it appears, some disturbing influence introduced along with the causes which increase the intensity of the lines. This disturbing influence retards the rate of vibration, and its effect becomes more marked as the atomic mass increases. It is now possible to determine the amount of the disturbance produced in this way, and to compare it with the disturbance produced by increases in the atomic mass.

The metals of the alkalis have closely allied chemical and physical properties; but the three metals, potassium, rubidium, and caesium, are more closely related to one another than to lithium and sodium. The spectra of these three metals may be said to agree almost line for line, but the spectra of lithium and sodium are moved considerably towards the more refrangible end of the spectrum: the corresponding vibrations are much faster in lithium and sodium. The effect of increase of atomic mass in these groups is to diminish the oscillation frequency of the lines, and the rate of change is much greater in passing from lithium to sodium and potassium than from potassium to rubidium and caesium.

These facts appear to indicate that there is something besides the molecule of the element involved in the production of the lines under consideration. The late Professor Rowland remarked, in an address on "The Highest Aim of the Physicist"\*:—"We know of little or no etherial disturbance which can be set up by the motion of matter alone: the matter must be electrified, in order to have sufficient hold on the ether to communicate its motion to the ether." This fact suggests the view that the influence outside the molecule is the portion of the æther affected by the motion of the electrified molecule: that this portion of æther acts as a load on the molecule (or it may be that the molecule acts as a load on the æther), the effect in the end being that the spectral lines in the series we have been considering are produced by the mutual action of the matter and the æther.

This suggestion seems to offer an explanation for the retardation which increases with the intensity of the members of the series. It would appear that the intensity of the line is proportional to the amount of the æther affected, and as the load is greater so is the retardation of the vibrations greater.

\* 'Amer. Jour. Sci.,' December, 1899, p. 406.

A supposition such as the above would imply that one molecule can produce only one line at a time. Lord Rayleigh\* has already made a suggestion of this nature in discussing a formula deduced theoretically. He wrote:—"In this case instead of supposing that the whole series of lines correspond to various modes of one highly compound system, we attribute each line to a different system vibrating in a special mode."

The data available at present are far from complete, and some of the suppositions are open to question. For instance, the value of  $N_0$  is adopted from the formula for hydrogen, without considering the influence of its atomic mass. Although the effect of this mass may be small, it may be sufficiently great to complicate the results calculated from it, so as to obscure a regular order in the changes produced by the increase in the masses of the elementary substances.

An article by Professor Pickering† on "The Spectrum of  $\zeta$  Puppis," contains statements which confirm the views expressed above regarding the formula of Kayser and Runge. He has found that a slight modification of Balmer's formula  $3636 \cdot 1 \left( \frac{n^2}{n^2 - 16} \right)$ , gave the lines of the ordinary series of hydrogen and the additional series more accurately than Kayser's formula,  $\frac{1}{\lambda} = A + B \frac{1}{m^2} + C \frac{1}{m^4}$ . He remarked: "On the whole, the observed values agree more nearly with the first formula than with the second. This is remarkable, if it does not represent the true law, since this formula contains no arbitrary constants."

*A Comparative Study of the Densities and Melting Points of some Groups of the Elements.*

The graphical method, employed in the investigation of spectra, has been extended to two other properties of the elements—density and melting point. These properties were chosen because the data concerning them were more complete than the data relating to other properties.

It is hoped that the graphical method of investigation may, as time and data permit, be extended to the other properties of the elements. We have observed that the shift of some of the lines in spectra is proportional to the atomic mass; of others, to the square of the atomic mass. The proposed extension of the work will tell us which properties of the elements follow the first order, which follow the second, and possibly of some which vary with some other power or function of the atomic mass. Such information will doubtless throw considerable

\* 'Phil. Mag.,' vol. 44, p. 361, 1897.

† 'Astrophys. Jour.,' April, 1901, p. 232.



light on the fundamental causes of the properties of matter. The method will also be applicable to the study of compounds.

Three diagrams have been drawn and studied. They were drawn as follows :—

| Abscissæ.                                                                                        | Ordinates.                    |
|--------------------------------------------------------------------------------------------------|-------------------------------|
| (a) Densities.                                                                                   | Atomic masses.                |
| (b) Melting points.                                                                              | " "                           |
| (c) Densities and melting points of the elements whose spectra have been studied by this method. | Squares of the atomic masses. |

*Diagrams (a) and (b).*—The positions of similar elements on these diagrams may be connected by lines which resemble in form those which connect the spectra. In some groups the breaks in the lines are less marked, while in others they are more marked than in the spectra.

The changes in the diagram involving density are more regular than the changes in those involving melting points. In both of the first two diagrams lithium, beryllium, boron, and carbon lie on lines which are nearly straight.

*The Metals of the Alkalies.*—There is a decided break in the density diagram between sodium and potassium. A single smooth curve can be drawn through the five metals on the melting point diagram: its form and direction would be similar to those of the line joining the ends of the series in the diagram of spectra, Plate I, of these elements.

*Copper, Silver, and Gold.*—Both the curves joining these metals are remarkable. The connection between the densities of sodium and copper is quite in agreement with those between magnesium and zinc, aluminium and gallium, &c. The angles which the successive lines make with the horizontal increase from the sodium-copper line to the silicon-germanium line.

There is thus an interesting double connection from sodium to potassium on the one hand, and to copper on the other.

*Beryllium, Magnesium, Zinc, Cadmium, and Mercury.*—The connections drawn between these are regular; from magnesium upwards the two curves are approximately symmetrical.

*Beryllium, Magnesium, Calcium, Strontium, and Barium.*—The connecting lines are only slightly curved. The melting points of strontium and barium are not known accurately: those recorded place them on a slightly curved line which passes on to beryllium.

The double connection from magnesium to calcium and to zinc is another interesting feature.

*Boron, Aluminium, Gallium, Indium, and Thallium.*—There is a break

in the density curve above aluminium, and the curve joining the metals above is nearly a parabola. In the melting point curve, boron, aluminium, and gallium are nearly on a straight line; the curve then takes a totally different form. This break corresponds to the break in the diffuse series of the spectra, so that the same fundamental causes appear to act in the production of these series, and in determining the densities and melting points of the elements. It will be an interesting study to trace those properties of the elements which vary regularly from aluminium to thallium in the way that the sharp series vary.

*Silicon, Germanium, Tin, and Lead.*—The connecting lines between these elements are peculiar. There is a suggestion that the density of germanium is too low: the diagram indicates that it should be between 5.8 and 5.9 instead of being 5.47. We observe, also, that the melting point is remarkable. If this followed the order of the other cases studied it would be below the melting point of tin. It is possible, therefore, that germanium is a peculiar element, and worthy of more complete investigation. From carbon the melting point falls with increase in the atomic weight until tin is reached; and it is only then the change of direction takes place, one stage later than in the other groups.

*Diagram (c).*—Three of the long connecting lines approach to straight lines in this diagram: those in both density and melting point diagrams for zinc, cadmium, and mercury, and that in the density diagram for gallium, indium, and thallium. The first of these three lines is almost perfectly straight, and the densities may be calculated from an equation containing the square of the atomic mass:  $\text{Density} = 6.38 + 1803 W^2 \times 10^{-7}$ . This formula gives zinc and mercury correctly, and cadmium 0.01 too high.

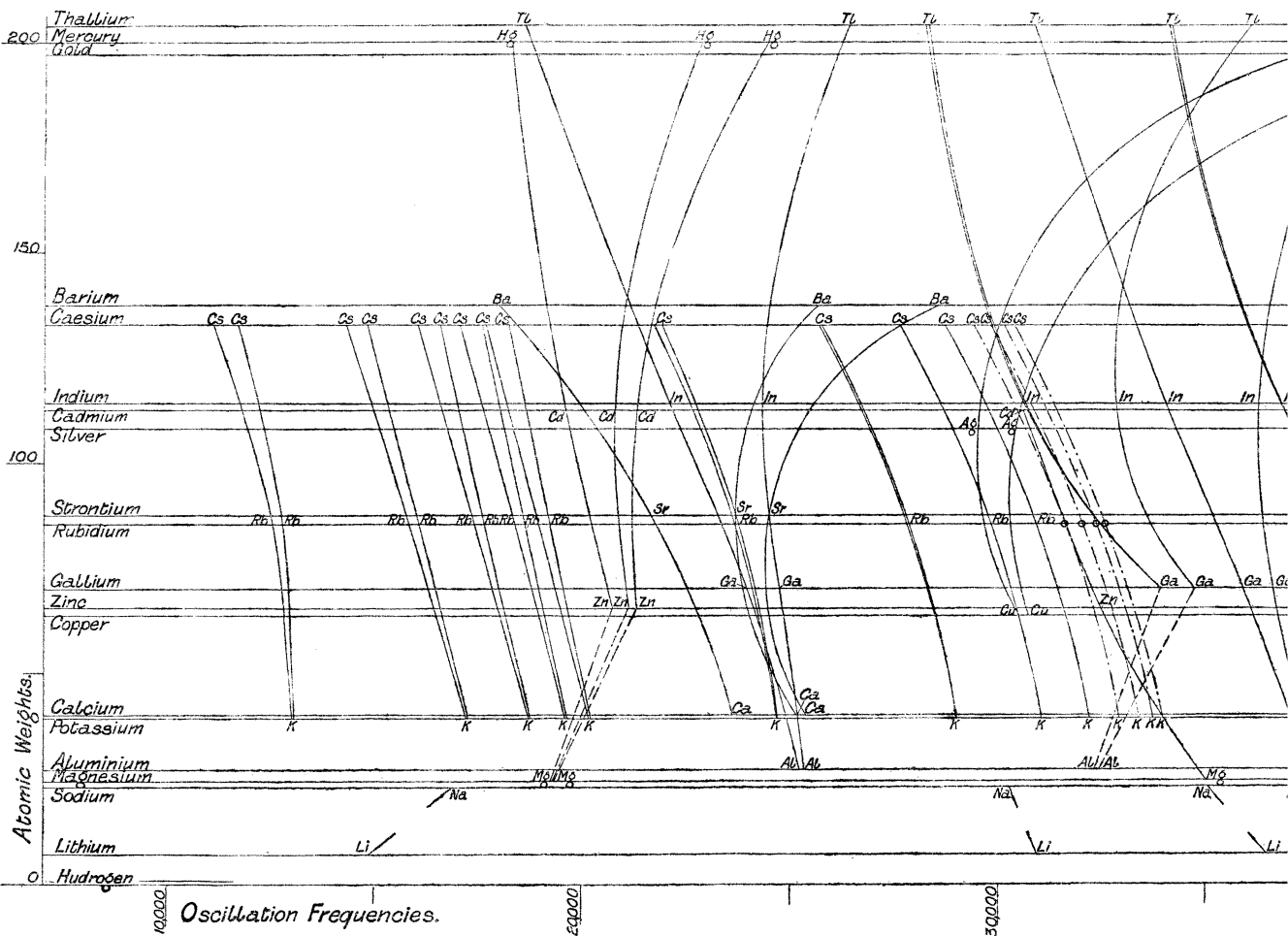
### Conclusions.

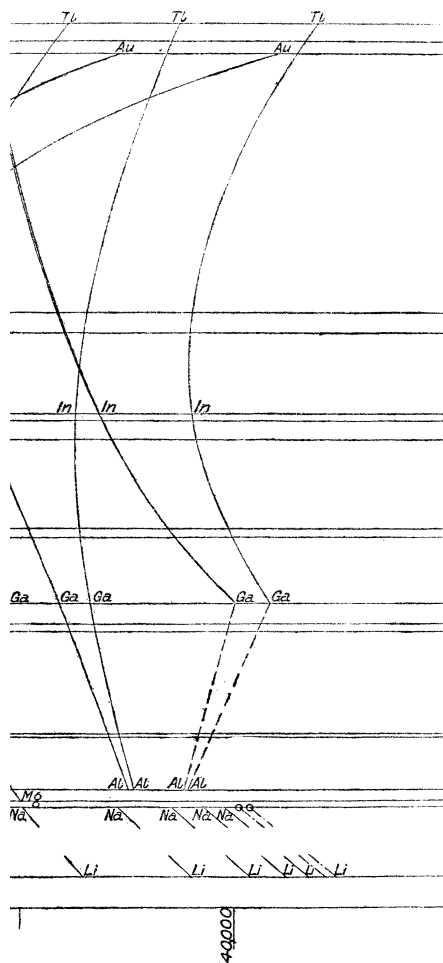
It has been usual for investigators to rest satisfied when the properties of the elements were shown to be “a periodic function of the atomic mass.” Diagrams drawn, by the method employed in this paper, of each of the properties of the elements will show in what degree the properties vary with the atomic mass, and will make it easier to establish the exact quantitative relations.

The work and results now presented indicate that the properties of the elements are fundamentally due to the structure of the atoms, as revealed by their spectra, rather than to the quantity of matter in them. It seems, for instance, inconceivable that the transition from calcium to strontium proceeded through the intermediate elements, when we consider that the strontium molecules must have a similar structure to those of calcium. This structure is so simple that the fundamental (Bunsen flame) spectrum of each of these elements consists of a single line. The anomalies, according to Mendeléeff’s law, in the atomic

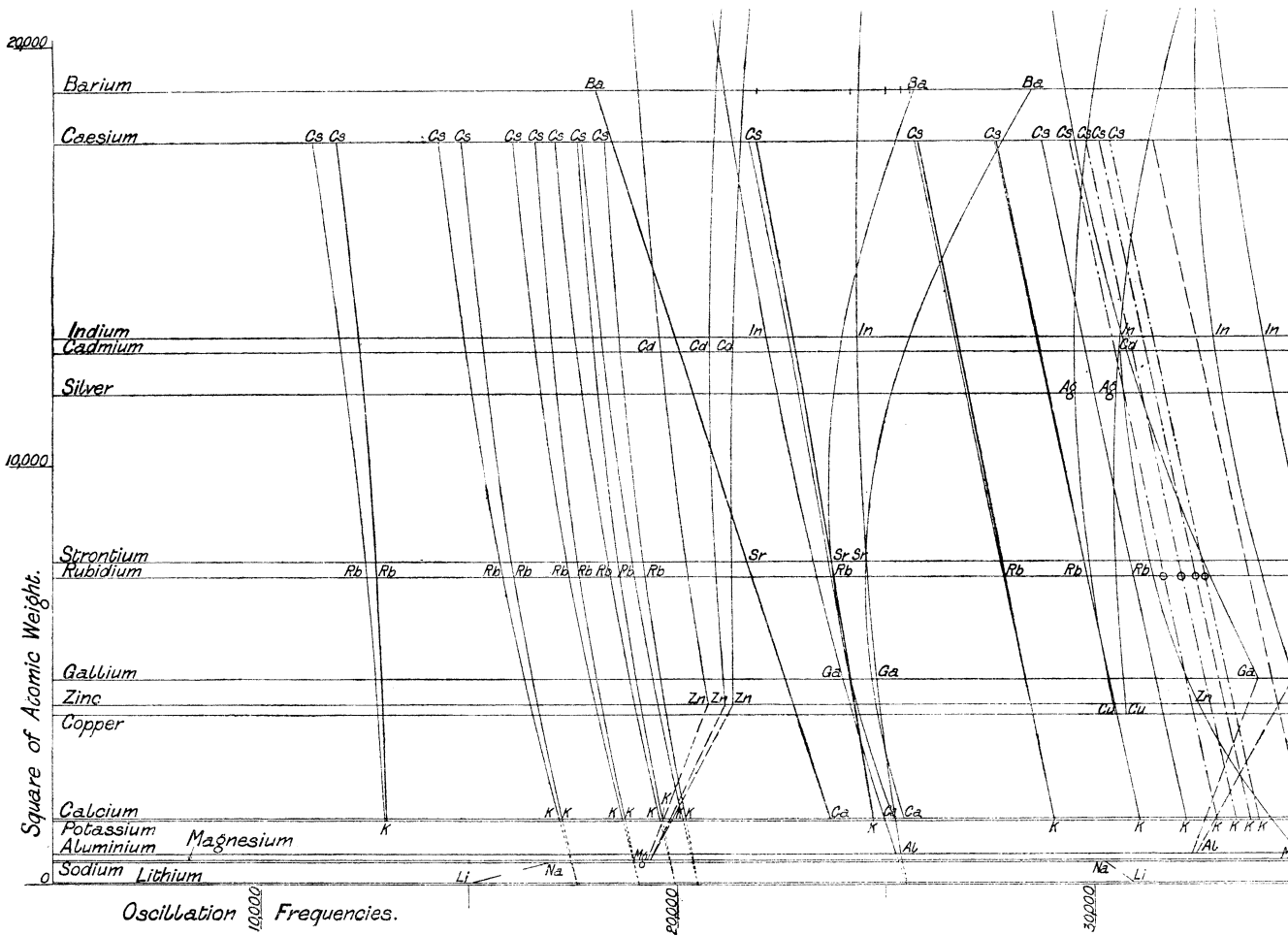
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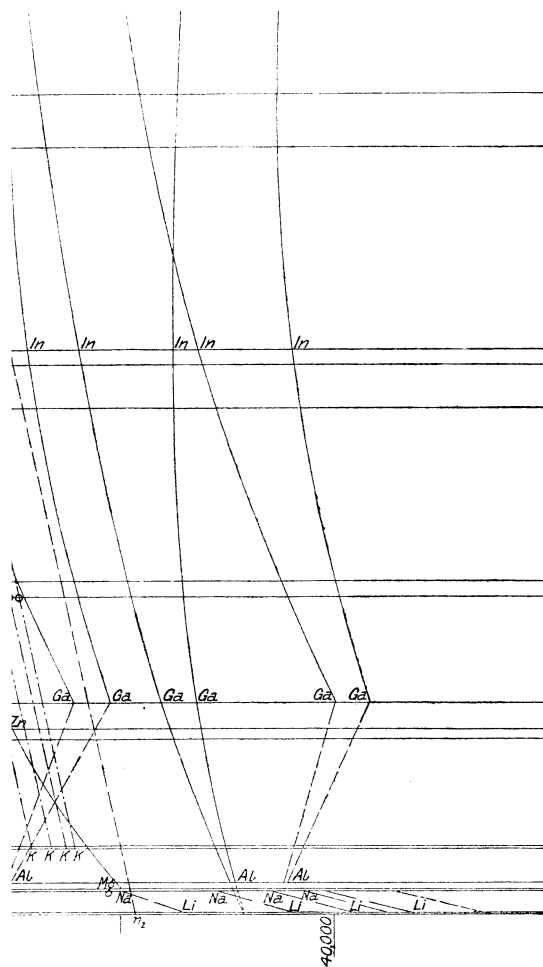
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masses of tellurium and iodine, &c., are further evidences of this. The properties of tellurium and iodine may have nothing whatever to do with each other. They are, however, closely related to, and in correct order with, those of the elements of their respective groups as given above. The genesis was not in the direction of tellurium to iodine, but from, or perhaps through, oxygen and fluorine respectively. So also with regard to the other groups.

It is more probable that in the genesis of the elements the properties of certain fundamental substances are modified by successive additions of matter to them,\* or by causes of which this is, to us, the apparent result. The regularity in the changes in the properties of lithium, beryllium, boron, and carbon, as seen in the diagrams, is very remarkable. It is, furthermore, very suggestive, for the changes in properties are approximately proportional to the quantity of matter in the atom in excess of a constant (which is about 6), as if it were the same matter that is added in each case.

I must express my best thanks to Dr. J. H. Vincent, to Professor Liveing, Dr. Larmor, and Professor J. J. Thomson, for the interest they have taken in this work, and for the kindly encouragement they gave me, especially in the earlier stages of it. It was while working with Professor Hartley that I acquired the knowledge of spectra which led me to begin the investigation, and I am deeply grateful to him for the means of acquiring that knowledge.

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“Experimental Researches on Drawn Steel.—Part I. Magnetism and its Changes with Temperature.—Part II. Resistivity, Elasticity and Density, and the Temperature Coefficients of Resistivity and Elasticity.” By J. REGINALD ASHWORTH. Communicated by Professor SCHUSTER, F.R.S. Received January 30,—Read March 6, 1902.

(Abstract.)

#### PART I.

In a former paper it was shown that the variation of the intensity of magnetisation of a magnet under fluctuations of temperature is controlled to a large extent by the self-demagnetising factor of the

\* *January 27, 1902.*—Professor Hartley has recently called my attention to a letter “On the Inadequacy of Aids and Facilities for Scientific Research,” which he wrote to the ‘*Chemical News*’ on November 9, 1895. The following statement is quoted from that letter:—“One element in a group differs in its properties from another, not because it consists of another kind of matter, but because the quantity of matter in an atom of it is different.”

