

VIII. *A Critical Study of Spectral Series.—Part III. The Atomic Weight Term and its Import in the Constitution of Spectra.*

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ABBREVIATIONS.

[I.] and [II.] denote the two previous parts of this discussion published respectively in the ‘Phil.

Trans.,’ A, vol. 210 (1910), and vol. 212 (1912).

The formula for a line is $n = N/D_1^2 - N/D_m^2$.

N/D_1^2 is the limit or value when $m = \infty$.

ξ denotes the correction to be added to any limit adopted to give the true value.

N/D_m^2 is referred to as the V part (variable).

D_m is referred to as the denominator of the line.

“Separation” of two lines is the difference of their wave numbers.

“Difference” of two lines is the difference of their denominators.

“Mantissa” is the decimal part of the denominator.

ν denotes the separation of two lines of a doublet.

Δ is used for the denominator difference of the two lines which produces ν .

$\nu_1, \nu_2, \Delta_1, \Delta_2$ are similar quantities for triplets.

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W denotes the atomic weight, $w = W/100$.

δ_1 denotes the "oun" = $90 \cdot 47w^2$.

$\delta_n = n\delta_1$, but δ is used for $\delta_4 = 361 \cdot 89w^2$.

O - C is used for the difference in wave-length between an observed line and its calculated value.

O denotes the maximum possible error of observation.

In general, figures in brackets before lines denote intensities, and in brackets after, possible errors of observation.

THE doublet and triplet separations in the spectra of elements are, as has long been known, roughly proportional to the squares of their atomic weights, at least when elements of the same group of the periodic table are compared. In the formulæ which give the series lines these separations arise by certain terms being deducted from the denominator of the typical sequences. For instance, in the alkalis if the p -sequence be written N/D_m^2 , where $D_m = m + \mu + \alpha/m$, the p -sequence for the second principal series has denominator $D - \Delta$, and we get converging doublets; whereas the constant separations for the S and D series are formed by taking $S_1(\infty) = D_1(\infty) = N/D_1^2$ and $S_2(\infty) = D_2(\infty) = N/(D_1 - \Delta)^2$. It is clear that the values of Δ for the various elements will also be roughly proportional to the squares of the atomic weights. For this reason it is convenient to refer to them as the atomic weight terms. We shall denote them by Δ in the case of doublets and Δ_1 and Δ_2 in the case of triplets, using ν as before to denote the separations. Two questions naturally arise. On the one hand what is the real relation between them and the atomic weights, and on the other what relation have they to the constitution of the spectra themselves? The present communication is an attempt to throw some light on both these problems.

The Dependence of the Atomic Weight Term on the Atomic Weight.

The values of the Δ can be obtained with very considerable accuracy, especially in the case of elements of large separations, *i.e.*, of large atomic weight. If, therefore, the definite relation between these quantities can be obtained, not only may it be expected to give some insight into the constitution of the vibrating systems which give the lines, but it may afford another avenue whereby the actual atomic weights of elements may be obtained, and the solution of the problem is therefore of importance to the chemist as well as to the physicist.

It may be interesting to note the steps which first led the author to the solution which follows, and incidentally may add some weight to the formal evidence in its favour. It has long been known that in the case of triplets the ratio of $\Delta_1 : \Delta_2$ is always slightly larger than 2. It was natural, therefore, in an attempt to discover their relation to the atomic weight to consider the values of $\Delta_1 - 2\Delta_2$. These were calculated for several cases, Δ_1 and Δ_2 being expressed in terms of the squares of the atomic weights. It was at once noticed that in several cases these differences were multiples of the same number, in the neighbourhood of 360, *e.g.*, Ca 1, Sr 3, Ba 8,

Hg 19, and, further, that in many cases Δ_1 and Δ_2 were also themselves multiples of the same number. As, however, Mg with a difference of 450 and Zn of 543 could not possibly be brought into line with the others, this line of attack was given up. But later the case of Zn, which at first had seemed to stand in the way of an explanation on these lines, gave cause for encouragement. The series for Zn are well defined, the measures good, and the formulæ reproduce the lines with great accuracy.* Great confidence can thus be put in the values for Δ_1 and Δ_2 , and it was noticed that they were both extremely exact multiples of the difference $\Delta_1 - 2\Delta_2$. In fact, the values are $\Delta_1 = 31 \times 543 \cdot 446w^2$ and $\Delta_2 = 15 \times 543 \cdot 476w^2$. This relation could hardly be due to mere chance, especially when it was also noticed that 543.44 is very close to $3/2$ the former 360, and, further, the 450 of Mg is about $5/4$ the same. In other words, with the rough values used $360 = 4 \times 90$, $450 = 5 \times 90$, and $540 = 6 \times 90$. This looked so promising that a systematic discussion of all the data at disposal with limits of possible variation was undertaken. The theory to be tested then is that the Δ of any element which give its doublet or triplet separations are multiples of a quantity proportional to the square of the atomic weight. We will denote this by $\delta = qw^2$. It will be convenient, in general, to deal with the 360 quantity, and δ will be used to denote this. If other multiples are dealt with as units a subscript unit will be used giving the multiple of the 90. Thus δ_1 denotes the smallest, $\delta_6 = 542 \cdot 7w^2$, and so on. The results are given in Table I. below.

The value of Δ is obtainable as the difference of two decimals with six significant figures. It is convenient therefore to tabulate the values of $10^6\Delta$. The exactness of the calculated value depends on (1) the correctness of the adopted value of $S(\infty)$, (2) the exactness with which ν is measured, and (3), when expressed in terms of w^2 , the exactness of the value of W or the atomic weight. In the case of the latter the value $W/100 = w$ is used and the values of $10^6\Delta/w^2$ are tabulated. The method adopted may best be seen by taking an actual example, say that of calcium. The values of ν_1, ν_2 as found by least squares from the S-series are 105.89, 52.09. The value of $S(\infty)$ as given in Table I. of [II.] is 33983.45, and the correct value is supposed to be ξ larger. The numbers 33983.45, 34089.34, 34141.43 are then thrown into the form N/D^2 , and the denominators are 1.796470, 1.793679, 1.792310, giving for differences $\Delta_1 = .002791$, $\Delta_2 = .001369$, which are tabulated as 2791, 1369. The corrections for the error ξ are found to be $-.2\xi$ and $-.1\xi$. Moreover, the last digits of 10^6D may be .5 wrong and the value of the Δ be ± 1 out. In cases where the ν are known to three decimal places, the calculations are carried out with 9-figure logarithms, and the values of Δ determined without this ambiguity. The values of ν may be wrong by $d\nu$, *i.e.*, $105.89 + d\nu$, &c. This will produce a variation in Δ_1 of $26.3d\nu$ —in general $d\nu$ is a fraction $< .1$. Thus

$$\Delta_1 = 2791 \pm 1 - .2\xi + 26.3d\nu.$$

* See Table I. of Part II.

The atomic weights are supposed to be those given by BRAUNER,* $+x$, where x is a number to be added to the fourth significant figure in BRAUNER'S value. BRAUNER gives for Ca 40.124. Δ_1 is then divided by $(.40124)^2$.

The result is

$$\Delta_1 = (17336.1 \pm 6.22 - 1.24\xi + 163dv_1 - 8.64x)w^2.$$

This is

$$= 48 (361.169 \pm .13 - .025\xi + 3.4dv_1 - .180x)w^2.$$

Table I. gives the values for those elements in which the series have been established. The second column contains the atomic weight as given by BRAUNER, except for the few belonging to volumes of ABEGG'S 'Handbuch' not yet published, with estimated possible error beneath. In the third column the top number gives ν and the second $10^6\Delta$. For triplets there are therefore two sets. The fourth column gives $10^{10}\Delta/w^2$, and the multiples of which it is composed. In general the 360 ratio is taken, but in several cases it is necessary to take 2×90 or 180 and 1×90 . The second line of columns 5, 6, 7, 8 gives the coefficient of the error corrections to be applied to this number 360, or 180, &c., as the case may be, and the upper line of figures gives the maximum errors estimated, which have, in general, been less than those permissible by the observations. The last column gives the difference between 361.8 and the factor given in the fourth column, except that when it is not the 4×90 term it is brought up to it by multiplying by 2 if it is 180 and 4 if 90. The maximum errors are also attached.

In many cases it will be seen that the number of significant figures in the calculated numbers is larger than in the data from which they are derived. In these cases the number of significant figures in the data must be supposed to be made up to the proper number by the addition of zeros. This enables new calculated values to be determined when the data are improved without the trouble of recalculation.

TABLE I.—Evaluation of δ and of m .

Notation.— W = atomic weight; $qw^2 = \delta$ with $w = (\text{atomic weight})/100$; ξ , error in n_∞ ; dv , error in ν ; x , error in w on the fourth significant figure.

| | W. | ν , $10^6\Delta$. | qw^2 , $m\delta$. | ± 1 . | $-\xi$. | dv . | $-x$. | 361.8 +. |
|----|-------------|------------------------|--------------------------------|-----------|-----------|------------|------------|-------------|
| Na | 22.998 2 | 17.175 743.0 | 14027.96 155 \times 90.50 | 0 0 | 1 .021 | 0 5.21 | .2 .078 | .2 .141 |
| K | 39.097 3 | 57.87 2939 | 19224.86 53 \times 362.72 | .012 | 1 .037 | .5 6.26 | .3 .142 | .92 3.22 |

* ABEGG, 'Handbuch der Anorganischen Chemie.'

TABLE I. (continued).

| | W. | ν , $10^6\Delta$. | qw^2 , $m\delta$. | ± 1 . | $-\xi$. | dv . | $-x$. | $361\cdot 8+$. |
|----|--------------|--|--|-----------------------|----------------------|----------------------------|--------------------|------------------------------|
| Rb | 85·448 5 | 237·54 12935 | 17715·86 $49 \times 361\cdot 40$ | ·003 | 1 ·022 | ·3 1·52 | ·5 ·084 | -·40 ·56 |
| Cs | 132·823 7 | 553·80 32551 | 18449·48 $51 \times 361\cdot 74$ | 0 | 1 ·025 | ·4 ·65 | ·07 ·96 | -·06 ·33 |
| Cu | 63·56 1 | 248·49 7311 | 18075·8 $50 \times 361\cdot 84$ | ·05 | 5 ·02 | ·4 1·44 | 1 ·115 | ·04 ·80 |
| Ag | 107·88 | 920·61 27791 | 23879·34 $66 \times 361\cdot 81$ | ·006 | 10 ·017 | ·02 ·39 | 0 ·33 | ·01 ·2 |
| Au | 197·20 7 | 3815·52 $113961 + 31y$ | $81 \times 361\cdot 80$ | | | | | |
| Mg | 24·362 2 | 40·90 854 19·89 415 $\Delta_1 + \Delta_2 =$ | 14389·05 $159 \times 90\cdot 497$ 6992·33 $77 \times 90\cdot 89$ $59 \times 362\cdot 36$ | 16·91 ·423 ·219 | 3 ·010 ·003 | ·02 8·79 ·04 4·57 | 5 ·075 ·075 | ·19 1·78 3·12 |
| Ca | 40·124 5 | 105·89 2791 52·09 1369 $\Delta_1 + \Delta_2 =$ | 17336·1 $48 \times 361\cdot 169$ 8503·4 $47 \times 180\cdot 923$ $143 \times 180\cdot 696$ | ·129 ·129 | 6 ·025 ·013 | ·1 3·4 ·1 3·48 | 5 ·180 ·090 | -·63 1·52 -·24 1·00 |
| Sr | 87·66 3 | 394·35 11835 186·93 5533 $\Delta_1 + \Delta_2 =$ | 15401·6 $85 \times 181\cdot 195$ 7200·4 $20 \times 360\cdot 02$ $125 \times 180\cdot 82$ | ·015 ·065 | 4 ·008 ·019 | ·2 ·46 ·1 1·95 | 3 ·041 ·083 | ·59 ·72 -1·78 ·585 |
| Ba | 137·43 6 | 878·21 29328 370·33 11976 $\Delta_1 + \Delta_2 =$ | 15528·2 $43 \times 361\cdot 121$ 6340·96 $35 \times 181\cdot 170$ $121 \times 180\cdot 74$ | ·012 ·015 | 10 ? ·019 ·017 | ·2 ·41 ·2 ·49 | ·6 ·526 ·263 | -·68 ·600 +·54 ·882 |
| Ra | 226·4 | 2050·26 92658 832·00 ? 34390 $\Delta_1 + \Delta_2 =$ | 18077·15 $50 \times 361\cdot 543$ 6709·3 $37 \times 181\cdot 33$ $137 \times 180\cdot 92$ | ·004 | 10 ? ·023 | ? ·023 | ? ·32 | -·257 2 ? ·86 |

TABLE I. (continued).

| | W. | ν , $10^6\Delta$. | qw^2 , $m\delta$. | ± 1 . | $-\xi$. | dv . | $-x$. | $361 \cdot 8 +$. |
|----|-------------|--|--|-----------|---------------------|------------------------|--------------------|----------------------------------|
| Zn | 65·40 3 | 388·905 7204·42 190·093 3486·20 $\Delta_1 + \Delta_2 =$ | 16843·68 $31 \times 543 \cdot 334$ 8150·74 $15 \times 543 \cdot 383$ $46 \times 543 \cdot 356$ | 0 0 | 1 ·015 ·015 | 0 0 | 3 ·135 ·135 | ·423 ·420 ·456 ·420 |
| Cd | 112·3 1 | 1170·848 23105·56 541·892 10368·54 $\Delta_1 + \Delta_2 =$ | 18321·33 $101\frac{1}{2} \times 180 \cdot 504$ 8221·64 $91 \times 90 \cdot 348$ $49 \times 541 \cdot 50$ | 0 0 | ·3 ·007 ·003 | 0 ·15 ·16 | 1 ·321 ·160 | — ·8 ·646 — ·408 — ·644 |
| Eu | 151·93 3 | 2630·5 51223 1004 18329 $\Delta_1 + \Delta_2 =$ | 22191·06 $123 \times 180 \cdot 41$ 7940·57 $22 \times 360 \cdot 93$ $333 \times 90 \cdot 485$ | | 10? ·007 ·013 | 3 ·068 1 ·136 | ·3 ·236 ·472 | — ·98 ·68 — ·94 ·39 |
| Hg | 200·3 3 | 4630·648 87814·99 1767·01 30002·3 $\Delta_1 + \Delta_2 =$ | 21888·03 $121 \times 180 \cdot 892$ 7478·05 $83 \times 90 \cdot 096$ $54 \times 543 \cdot 816$ | 0 ·002 | 2 ·013 ·0026 | 0 ·078 ·3 ·05 | 3 ·354 ·091 | — ·015 2·12 — 1·41 1·15 |
| Al | 27·10 5 | 112·15 1754 | 23884 $66 \times 361 \cdot 879$ | ·21 | 3 ·012 | ·02 3·21 | 5 ·266 | ·079 1·635 |
| Ga | 69·9 3 | 826·10 13498 | 27715 $77 \times 359 \cdot 93$ | ·026 | 1 ·011 | ·10 ·435 | 30 ·103 | — 1·87 3·17 |
| In | 114·8 5 | 2212·38 37684 | 28593·88 $79 \times 361 \cdot 947$ | ·01 | 1 ·117 | ·25 ·165 | 5 ·630 | ·147 3·32 |
| Tl | 204·04 5 | 7792·39 134154 | 32223·62 $89 \times 362 \cdot 063$ | ·002 | 0 ·012 | ·03 ·047 | ·5 ·355 | ·263 ·18 |
| Sc | 44·1 5 | 320·80 7140 or 6404 | 36714 $101\frac{1}{2} \times 361 \cdot 714$ $91 \times 361 \cdot 89$ | ·05 | ·014 | 1 1·136 | 50 ·165 | — ·086 9·45 |
| He | 3·99 | 1·007 33·377 | 20860 $58 \times 361 \cdot 45$ | 0 | 0 | 0 ·355 | 5? ·180 | ·35 1 |

TABLE I. (continued).

| | W. | ν , $10^6\Delta$. | $q\nu^2$, $m\delta$. | ± 1 . | $-\xi$. | $d\nu$. | $-x$. | 361·8+. | |
|----|-------------------------|------------------------|-----------------------------------|-----------|----------|----------|--------|---------|-----|
| O | 16 | 3·65 | 6692 | 2·11 | 1·13 | ·03 | 0 | — | ·01 |
| | | 171·3 | $18\frac{1}{2} \times 361\cdot79$ | | | 100 | 0 | 5 | |
| | | 2·03 | 3714·9 | | | ·03 | | 1·0 | |
| | | 95 | $41 \times 90\cdot20$ | ·95 | ·34 | 25 | | | 2 |
| | | ·62 | 148 ₁ | | | | | | |
| | | 34 | | | | | | | |
| S | 32·07 | 17·96 | 10150·85 | ·35 | 10 | ·1 | ·226 | ·34 | 3 |
| | | 1044 | $28 \times 362\cdot14$ | | | ·019 | | 20·14 | |
| | | 11·21 | 6329·7 | ·21 | ·009 | 10·05 | ·113 | | 1·5 |
| | | 651 | $35 \times 180\cdot67$ | | | | | | |
| | $\Delta_1 + \Delta_2 =$ | $91 \times 181\cdot1$ | | | | | | | |
| Se | 79·2 | 103·70 | 10192 | ·057 | ·034 | ·2 | 20? | 2·20 | 3? |
| | | 6392 | $28 \times 364\cdot00$ | | | 3·5 | ·092 | | |
| | | 44·69 | 4363·4 | ·057 | ·04 | 4·08 | ·092 | 1·81 | 3? |
| | | 2737 | $12 \times 363\cdot61$ | | | | | | |
| | $\Delta_1 + \Delta_2 =$ | $161 \times 90\cdot40$ | | | | | | | |

Data on which the Table is based.

Na. The limit is 24476·11. It is the limit found in [I.] corrected by the result of ZICKENDRAHT'S measurements of the high orders of NaS. The value of ν adopted is that deduced from FABRY and PEROT'S interferometer measurements of the D-lines using 9-figure logarithms. Consequently, the results are more reliable than would otherwise be expected from such a low atomic weight. But on this point, see below (p. 331).

The limit for K is 21964·44—corrected from the value in [I.] by addition of 1·06 as indicated by ZICKENDRAHT'S observations. The value of ν is very ill-determined. A value of $\nu = 57\cdot73$ would make $q = 361\cdot80$. SAUNDERS' results for S (3) give $\nu = 57\cdot75$, and K.R.'s for S (4) give $57\cdot60 \pm \cdot30$. The value in the table is that used in [I.] $57\cdot87 \pm 1$. The limits for Rb and Cs are those given in [I.] for $S(\infty)$, viz., 20869·73 and 19671·48.

Cu. $S(\infty) = 31515\cdot48$.

Ag. $D(\infty) = 30644\cdot60$, found from first three lines. FABRY and PEROT have measured by the interferometer $D_{11}(2)$ and $D_{21}(2)$ and K.R.'s are extremely close to these. They have been taken as correct to $\cdot001 \text{ \AA.U.}$ The lines D_{12} and D_{11} are so close that their difference of wave number as given by KAYSER and RUNGE are probably of the same order of exactness. We may regard, therefore, K. and R.'s $D_{11} - D_{12}$ and F. and R.'s $D_{21} - D_{11}$ as quite exact up to the second decimal place. This gives $\nu = 920\cdot61$. It cannot be uncertain to more than a few units in the first decimal. A more correct value is obtained below (p. 404).

The limits of the 2nd and 3rd groups of elements are those given in [II.]. In the cases of Zn, Cd, Hg, the interferometer measurements of FABRY and PEROT are used, except ν_2 for Cd and Hg, with 9-figure logarithms in order to get an extra significant figure, their readings being reduced to ROWLAND'S scale by HARTMANN'S factor 1·000034. In these cases the values of ν may be taken as practically correct to $\cdot001 \text{ \AA.U.}$

For Sc, see Appendix I.

He. Limit given in [I.], which is practically exact. $\nu = 1.007$ is given by PASCHEN as a result of all his readings and is probably not more than .002 in error. Consequently, the numbers for He have weight in spite of its low atomic weight.

O. The limit is 23204.00. Although ν_1, ν_2 are known with fair accuracy, the possible proportional errors are considerable, so that the data have small weight. The limit for the doublet series is 21204 with $\nu = .62$. The values are still more indefinite.

S. Limit 20106. The D series give 20110. This gives a considerable range of uncertainty.

Se. Limit 19275.10. The atomic weights for O, S, and Se are those of the International Committee of 1910.

The table shows at once that the two groups which give doublet series agree in giving the Δ as multiples of a number close to $361.8w^2$. Group II., giving the triplet series, require in several cases multiples of $90w^2$ or $180w^2$. It is curious that the groups which first indicated this relation do not show it so markedly and with so little doubt as the doublet series, in which by themselves it would probably never have been noticed. There seems to be some kind of displacement with the middle lines of the triplets. If, for consideration, the values of $\Delta_1 + \Delta_2$ be taken, this irregularity disappears, and, moreover, with the larger observed quantities, the proportional errors will be less.

If we agree to look upon the 361 as the normal type, and for numerical comparison multiply the 90 by 4 and the 180 by 2, and, if further, the results are supposed to be weighted by the estimated limits of variation assigned in the last column of the table, the method of least squares gives for the value of $q = \delta/w^2$ —

| | | |
|------------------|-----------|----------|
| Group I. | | 361.900, |
| „ II. | | 361.720, |
| „ III. | | 362.051, |
| All three groups | | 361.890. |

In Groups II. and III. it is possible too much weight has been given to Hg, ν_2 , and Tl. We will take as the preliminary value for q that of silver, viz., 361.81, which is practically that of the general weighted mean. The true value cannot vary much from this—probably less than .2. With this, the subsidiary values become $180.90 \pm .1$ and $90.45 \pm .05$.

It is seen that in the doublet groups all the elements can come within this limit. In fact, with the exception of K and Ga, they come extremely close. Ga is spectroscopically uncertain as well as in its atomic weight, and the uncertainty of K is due to the uncertainty in its value of ν . In the triplet groups also, all calculated from $\Delta_1 + \Delta_2$ have possible variations which will bring them within, although the closeness is not so marked as for the doublet elements. The sequence formulæ are well established in Groups I. and III., but there are uncertainties in Group II. which yet require clearing up. In this relation also, the table shows slight regular variations as, e.g., Δ_1 and Δ_2 err from the general mean in different directions, but in these cases

the values of $\Delta_1 + \Delta_2$ come much closer to it. The values of $(\Delta_1 + \Delta_2)/w^2$ are therefore added to the table. It is clear, however, that when the spectroscopic observations are good, the relation here established will enable very accurate measures of the atomic weight to be obtained. In fact, with the possible accuracy attainable in spectroscopic measurements, it may be hoped to obtain far more reliable values of these constants than by weighing, except in those cases where they are small. The table, for example, affords considerable support for BRAUNER'S estimates, except, possibly, in the Mg group, where the irregularities are due to spectral causes. The case of Zn may be taken as an example here. Its spectral values are very good, it shows with $w = 65.40$ the multiple 543.357 instead of $542.70 \pm .30$. If the excess is due to the value of the atomic weight, it should be .048 larger, which would be allowable within BRAUNER'S estimates to bring it to the adopted value of q , *i.e.*, $w = 65.448$. This is more fully considered below. The numbers for Se also seem to show that 79.2 is too small for its atomic weight. 79.40 would make q for $\Delta_1 = 362.16$ and for $\Delta_2 = 361.77$, and the spectral uncertainties would account for the outstanding differences.

If δ_1 is written for $\frac{1}{4}\delta$, it may be noticed that the values of the Δ for the first of each sub-group may be written—

| i. | | ii. | | iii. | | vi. |
|---------------|-----------------------|-----------------------|-----------------------|-----------------------|-----------------------|-----------------------|
| Na. | Cu. | Mg.* | Zn. | Sc. | Al. | S. |
| $155\delta_1$ | $50 \times 4\delta_1$ | $32 \times 5\delta_1$ | $31 \times 6\delta_1$ | $52 \times 7\delta_1$ | $33 \times 8\delta_1$ | $8 \times 14\delta_1$ |

and, moreover, the same multiples of δ_1 recur in several of the same group, *e.g.*, $\Delta_1 + \Delta_2$ for Zn, Cd, and Hg, and Δ_1 for Eu are all multiples of $6\delta_1$, also the $5\delta_1$ occurs in Mg, Sr, Ba, and Ra. Analogy would lead to a corresponding $3\delta_1$ for Na. The values of the atomic weight and the doublet separations of Na are known with great accuracy, and no possible value given to ξ could change the multiple from 155 to 156 or 153. The only loophole for an explanation may be that the value of ν as found by FABRY and PEROT comes from the Principal series, and that $VP_1(1)$ is not really $S(\infty)$. This latter point has been discussed in [I.] and also in [II., p. 38]. It is equivalent to a considerable change in $S(\infty)$. To obtain a value 156 or 52×3 would require an increase of .07 in ν , *i.e.*, to 17.25. Such a value would be quite well in consonance with the measures of SAUNDERS and of K. and R. for other doublets, *e.g.*, D(2) 17.30 (S.), S(3) $17.22 \pm .26$ (K.R.), S(4) $17.05 \pm .38$ (K.R.), P(1) 17.20 (K.R.). But FABRY and PEROT'S values for P(1)—independently verified by Lord RAYLEIGH—would seem conclusive against this value, unless F. and P.'s apply only to VP(1) and 17.25 to $S(\infty)$. This would correspond to a lateral displacement of δ_1 (see below) between VP(1) and $S(\infty)$.

S and Se both give $8 \times 14\delta_1$ which falls in line with the other sub-groups. In fact,

* This is the value first deduced when the international system of atomic weights was used. It is δ_1 more than that in the table. The question is considered below.

if n denote the order of the group, the sub-groups would be based on $(2n+1)\delta_1$ and $(2n+2)\delta_2$. This would leave δ_1 and $2\delta_1$ for group 0. He, as is seen, may be either.

The foregoing evidence is, I think, conclusive that the atomic weight terms are multiples of a quantity very close to one quarter of $361.8w^2$. Before attempting on existing knowledge to obtain a closer value to this quantity, it will be desirable to consider certain other ways in which the atomic weight plays a part, and which will provide further data for its more exact determination. As it will be convenient to have a name for these quantities which seem to have a real existence, the word "oun" $(\omega v)^*$ is suggested.

The curious irregularities in the value of the oun noticeable in the elements of the 2nd group in connection with the separate Δ_1 and Δ_2 values, whilst the values found from $\Delta_1 + \Delta_2$ are normal is worth examining in closer detail. The values of $\nu_1 + \nu_2$ given in the table are deduced from the sums of ν_1, ν_2 , each determined independently by least squares from the best observations. If the values of $\nu_1 + \nu_2$ are determined directly the values are slightly different, which is natural as they are found from selected pairs. The old values and the values thus found are collected here, and with them the values of δ/w^2 .

| | Mg. | Ca. | Sr. |
|---------------|------------------|------------------|------------------|
| New | 60.79 (362.36) | 158.01 (361.45) | 581.21 (361.60) |
| Old | 60.79 (362.36) | 157.98 (361.39) | 581.28 (361.64) |
| | Ba. | Ra. | Zn. |
| New | 1248.85 (361.56) | 2882.26 (361.84) | 578.998 (362.23) |
| Old | 1248.54 (361.48) | 2882.26 (361.84) | 578.998 (362.23) |
| | Cd. | Eu. | Hg. |
| New | 1712.84 (362.41) | 2634.5 (361.94) | 6397.53 (362.46) |
| Old | 1712.74 (362.39) | 2634.5 (361.94) | 6397.66 (362.57) |

It will be shown later that spectroscopically Mg belongs rather to the Zn sub-group than to the Ca. The same tendency is exhibited here. The more probable values of $\nu_1 + \nu_2$ have brought the oun more closely to equality with $361.60w^2$ for the Ca sub-group, and with 362.4 for the Mg and the Zn sub-group. The value of ν_1 for Eu may be 2633.5 instead of 2630.5, and if so, its value of the oun would come to 362.34. If the variations in the value of the oun had been more irregularly distributed, it might have been natural to assign the variations (small as they are) to errors in the value of the atomic weight. But this does not seem justified unless there are chemical reasons whereby atomic weights in any particular group have a liability to be all over-estimated or all under-estimated. In view of the latter

* The pronunciation of oun will be the same in the chief European languages.

possibility it may be well to determine the amount of such error required to bring, say, the value 362.4 to 361.8, and 361.6 to 361.9, as it is probable the true value of the ratio lies between 361.8 and 361.9. The former requires an increase in atomic weight of $\frac{1}{1200}$, and the latter a decrease of $\frac{1}{2400}$ of the accepted values. The following would be the changes in atomic weight required:—

| Ca. | Sr. | Ba. | Mg. | Zn. | Cd. | Hg. |
|--------|--------|--------|--------|-------|-------|------|
| -0.025 | -0.036 | -0.052 | +0.02; | +0.04 | +0.09 | +0.2 |

According to the estimates of accuracy given by BRAUNER the changes for Mg and Ca are quite impossible, for Zn just possible, and for the others possible. In the case of Mg and Ca, however, small errors in $\nu_1 + \nu_2$ are considerable proportional errors and the deviations may be caused by these. It is necessary to have these estimates before us. Notwithstanding them, the close agreement of the numbers in each set, and the difference between the two sets must produce the conviction that the differences are real, and are not due to errors either in the spectroscopic measurements or the atomic weight determinations.

In the table the multiples given are those which give the ous most closely. An inspection, however, shows that in each element there is some disturbing influence affecting the Δ_1 and Δ_2 in opposite directions. Moreover, the sum of the multiples chosen are in certain cases not the multiple taken for $\Delta_1 + \Delta_2$, and this should clearly be so. This happens in Cd, Eu, and Hg. There is apparent a general rule that ν_1 is too small and ν_2 is too large, the deviation increasing with the atomic weight. The discrepancy is equivalent to a transference from the true Δ_1 to the true Δ_2 . Evidently the transfer in Cd, Eu, and Hg has been so large as to increase Δ_2 by more than δ_1 , so that the closest multiple now appears to be too large by unity. If the multiples in Δ_2 be diminished by unity, the sum is equal to that for $\Delta_1 + \Delta_2$, and the discrepancy between the ous from Δ_1 to Δ_2 increases in a regular order. A similar change has occurred in Sr, only here while the multiple of Δ_2 has apparently increased, that of Δ_1 has apparently decreased. If the ratio $\Delta_2 : \Delta_1$ be taken as 79 : 171 in place of 80 : 170 the discrepancy again falls into order with the others. With these changed ratios the values become

| | | |
|--------------|--------------|-------------|
| Sr | 171 × 90.068 | 79 × 91.144 |
| Cd | 203 × 90.252 | 90 × 91.351 |
| Eu | 246 × 90.205 | 87 × 91.27 |
| Hg | 242 × 90.446 | 82 × 91.17 |

This transference must take place in the $D_2(\infty) = S_2(\infty)$ term. The values are given in the following table in which the first column gives the value of $\Delta_2 : \Delta_1$, the second the value of the transference, the fourth the transference in ν_1 to ν_2 , the fifth the new value of Δ_2 , and the third and sixth are as explained later:—

| | $\Delta_2 : \Delta_1$. | dD . | $dD : \delta_1$. | $\delta\nu$. | Δ_2 . | δN . |
|----|-------------------------|----------|-------------------|---------------|--------------|--------------|
| Mg | 77 : 159 | ·96 | ·180 | ·05 | 414·0 | 0 |
| Ca | 47 : 96 | 1·9 | ·130 | ·05 | 1367·4 | 0·16 |
| Sr | 79 : 171 | 44·4 | ·639 | 1·49 | 5488·9 | 5·20 |
| Ba | 35 : 86 | 29·0 | ·1698 | ·90 | 11950·3 | 3·34 |
| Ra | 37 : 100 | 77·76 | ·1678 | 1·84 | 34312·2 | 8·13 |
| Zn | 15 : 31 | 0 | 0 | 0 | 3486·20 | 0 |
| Cd | 90 : 203 | 87·81 | ·7714 | 4·53 | 10282·7 | 11·86 |
| Eu | 87 : 246 | 157·8 | ·7577 | 8·53 | 18171·2 | 21·76 |
| Hg | 41 : 121 | 182·7 | ·5030 | 10·47 | 29817·7 | 25·64 |
| | | 82 : 243 | 274·46 | ·7563 | 15·72 | 29725·6 |

What is the nature of the modification? Perhaps the simplest explanation to test is that a fraction of δ_1 is transferred. The third column gives the fraction of δ_1 which is equal to the transfer. It is noticed at once that the two groups fall into two separate sets. With the exception of Sr, the fraction in the first is about ·17. Mg and Ca can both fit in with this, for the values are so small that they depend on decimals in the value of Δ_1 , Δ_2 , and therefore beyond our significant figures. In Ca, indeed, evidence is given later that Δ_2 is somewhat higher and would bring the ratio close to ·18. But Sr is quite out of step with the others. Zn has no transfer, Cd and Eu are equal, but Hg is 5030. If the ratio in Hg be taken to be 82 : 243 however, the fraction agrees with those of Cd and Eu. The Hg own is then $361\cdot43w^2$ in place of $362\cdot54$ and closer to the mean value, and as will be shown later there is evidence for the new value of Δ_2 (see p. 397). If this explanation is valid it must be possible to bring Sr into the scheme with a transfer of 11·7, but it is difficult to see how this can be done. ·639 is about four times too great, in other words, where the others are modified by a fraction of δ_1 , Sr is modified by the same fraction of δ . The above arrangement brings Mg into the Ca group and upsets the law whereby its first Δ_1 should be a multiple of $5\delta_1$. As this law seems to have a considerable weight of evidence in its favour, and moreover, as will be seen shortly, Mg tends to go spectroscopically with the Zn group, it may be well to see the result of keeping $\Delta_1 = 40\delta$ and the ratio $\Delta_2 : \Delta_1 = 19 : 40$. This will require a transfer of about 6·3 with a considerable uncertainty owing to the small values of Δ_2 and Δ_1 , and $\Delta_2 = 408\cdot7$. With this the fraction of δ_1 is 1·1727. To bring to the same fraction as in Cd the transfer should be about 4, which the uncertainty in 6·3 is not great enough to permit. As the fraction ·77 is of the order $1 - \frac{215}{m}$ it suggests that the modification is produced by adding δ_1 to the atomic volume term in the sequence of the P series, viz. (atomic weight term + δ_1) $\left(1 - \frac{215}{m}\right)$. The question must be left open at present. It has been noted that the arrangement which gives $\Delta_1 = 159\delta_1$ for Mg throws it out of the rule that the first members of the different groups are successive multiples of δ_1 . When the calculations were first made, the values of the

international atomic weights were used, and for Mg it is 24.32 in place of BRAUNER'S 24.362. This clearly gave $\Delta_1 = 160\delta_1$ and $\Delta_1 + \Delta_2 = 237\delta_1$ with $\delta = (362.09 \pm .65)w^2$ the uncertainty .65 not including that of atomic weight and being chiefly due to uncertainty in $\nu_1 + \nu_2$. The transference required now is 2.70, and the fraction of δ_1 is .502, again clearly not that of the Ca group, but when account is taken of the uncertainty in $\nu_1 + \nu_2$ quite possibly agreeing with that of the Zn group. The assumption that the international value of w is more correct than BRAUNER'S certainly gets over the difficulties mentioned above. But we are not justified in choosing the values from the particular systems which best suit our theories. The discrepancy between the international and BRAUNER'S is very great—from 10 to 15 times BRAUNER'S indication of his possible error.

Another suggestion as to a possible explanation may be given. There have been various indications in [I. and II.] that small variations in N may occur. If so it is possible to produce the changes observed by a small change δN in the middle line of the triplet. The necessary changes to do this are given in the sixth column. The changes clearly depend on the squares of the atomic weight, for if they are expressed in the form xw^2 they are

$$\begin{array}{ll} \text{Sr} \dots 5.20 = 6.767w^2 = 4 \times 1.564w^2 & \text{Cd} \dots 11.86 = 9.426w^2 \\ \text{Ba} \dots 3.34 = 1.777w^2 & \text{Eu} \dots 21.76 = 9.426w^2 \\ \text{Ra} \dots 8.13 = 1.586w^2 & \text{Hg} \dots 38.50 = 9.596w^2 \end{array}$$

in which it may be noticed that $9.426 = 6 \times 1.571$. Again multiples of a quantity depending on the square of the atomic weight enter, and it is especially interesting to note that the Zn group are affected with the multiple 6. If Ca and Zn show similar displacements, Ca would require $\delta N = .25$ in place of .16 and Zn 4.03. Zn is clearly 0, *i.e.*, is unaffected, but considering the small numbers involved in Ca and consequently large proportional errors, Ca might well show .25 instead of .16. The question naturally arises, do these quantities depend in any way on the own? Now any change in N may be supposed to arise either as a real change in N itself or an apparent change due to the introduction of a factor in connection with the $1/D^2$. In other words, the quantity VD is

$$N \cdot \frac{1+f}{(m+d)^2} \quad \text{or} \quad N \cdot \frac{(1+f)^2}{(m+d)^2}.$$

Looked at from this point of view, $9.426w^2$ requires $N(1 + .000859w^2)$ or $N(1 + .000429w^2)^2$. Now $5\delta_1$ would give $.000452w^2$, but if the present explanation is the true one, this is not a likely value since it will not include the alkaline earths. A value $6\delta_1 = .0005428w^2$ would be expected. The Ba value 1.777 would give $(1.000088w^2)$, or practically $(1 + \delta_1)^2$. It rather looks as if this explanation is a part of the truth. If more exact measures were at disposal it might be well to assume

these results as holding, recalculate for the denominators and discuss the rearrangement now required. It may be noted, however, that in the Zn sub-group a factor $(1+x\delta_1)^2$ in $D_1(\infty)$ would reduce the calculated one below $362.4w^2$ and $(1-y\delta_1)^2$ raise it in the Ca sub-group above $361.60w^2$ and at the same time increase the factors in the numbers above towards $(1+6\delta_1)^2$ and $(1+\delta_1)^2$. The factors may of course enter either as $(1+x\delta)^2$ or $(1-x\delta)^{-2}$.

Collaterals.

The first set in doublet or triplet S or P series is always the stronger. The others may be considered as receiving a sort of lateral displacement, by the atomic weight term, in the recognised way, and may be called collaterals. This kind of displacement is, however, not confined to the series generally recognised, but is of very common occurrence, and, indeed, depends not only on the Δ but also on other multiples of δ . In fact, the doublet and triplet series are only special cases of a law of very wide application. Some evidence of its existence will be given below. It will be sufficient now only to refer to certain points connected with the law, and to a convenient notation to represent it. This kind of relation was first noted in the spectra of the alkaline earths,* and as the lines are both numerous and at the same time strong and well defined, and, therefore, with very small observation errors, any arguments based on them must have special weight. Moreover, there are long series of step by step displacements involving large multiples of Δ between initial and final lines, so that we may feel some certainty that these large multiples are real and not mere coincidences.

As a compact notation is desirable the following has been adopted. In general† the wave number of a line is determined by a formula of the form $N/D_1^2 - N/D_m^2$, and lateral displacements may be produced by the addition (or subtraction) of multiples of δ , say $x\delta$ or $x\Delta$, to D_1 or D_m . This is indicated by writing $(x\delta)$ to the left of the symbol of the original line when it is added to D_1 , and to the right when added to D_m . Thus $\text{CaS}_1(2)$ is 6162.46. So far as numerical agreement goes 6439.36 is a collateral of this represented by $(2\Delta_1 + 10\Delta_2) \text{CaS}_1(2) (+\Delta_2)$. This means that whereas, see [II.],

$$\text{Wave number of CaS}_1(2) = \frac{N}{(1.796470)^2} - \frac{N}{(2.484994)^2},$$

$$\begin{aligned} \text{Wave number of 6439.36} &= \frac{N}{(1.796470 + 2\Delta_1 + 10\Delta_2)^2} - \frac{N}{(2.484994 + \Delta_2)^2}, \\ &= \frac{N}{(1.815732)^2} - \frac{N}{(2.486362)^2}. \end{aligned}$$

* A note on this relationship was given at the Portsmouth meeting of the British Association, see 'Report, B.A.' (1911), p. 342.

† Though not always, as I hope to show in a future communication.

Before going further it is desirable here to consider the nature of the cumulative effects produced by errors in the values of δ , or of the limits, in the course of a succession of step by step displacements. There may be a small error in the starting point, *e.g.*, $S(\infty)$ in the above example, or in the value adopted for ν . We will consider these separately, taking the case where the displacement is on the left, or the first term.

1. *The limit correct, but ν slightly too large.*—Then δ calculated from this is also slightly too large. It will, however, serve to identify a large series of steps in succession, *i.e.*, to reproduce the successive differences of the wave numbers of the lines. But the errors will all be cumulative, and if the last line of a set be calculated direct from the first, its denominator is too large and its wave number too small. In this case a more correct value of δ can be obtained by using these extreme lines, and this corrected value must satisfy all the other lines. In general a new correction will only affect an extra significant figure in the value of δ .

2. *δ correct, but limit wrong.*—In this case a slight error in the limit will be of no importance unless the δ and its multiples are considerable; and, as a rule, the limits are known with very considerable accuracy, except possibly in the alkaline earths and a few others. Let us suppose the limit adopted (say $S(\infty)$) is too large, that is, its denominator too small. If the second line is due to a positive displacement, its denominator is larger than that of the first, and the wave number less. Suppose D_1 , D_2 the denominators for the two lines, $D_2 > D_1$ if the displacement is positive, the separation is $N/D_1^2 - N/D_2^2$. If the limit is chosen too large D_1 and D_2 are chosen too small, although $D_2 - D_1$ is correct since δ is supposed correct. If D_1 becomes $D_1 - x$, the error in the separation is $2Nx/D_1^3 - 2Nx/D_2^3$, which is positive since D_2 is supposed $> D_1$, *i.e.*, the calculated separation is too large. If the displacement is a negative one, $D_2 < D_1$, the true separation is now $2N/D_2^2 - 2N/D_1^2$ and the error $2Nx/D_1^3 - 2Nx/D_2^3$, which is now negative since $D_2 < D_1$. The effect would be that in any series of step by step displacements δ would appear to require continual decreases, and at the end the "corrected values" would not at all fit the initial cases. If, then, it is found that when δ is corrected as in Case 1 the corrections tend to alter the former corrected one, and not to produce additional significant figures only, it may be surmised that the limit has been wrongly chosen. It is clear, then, that where there are a number of successive collaterals with a large multiple of δ between the extreme ones, we have at disposal a means whereby much more accurate values for δ and the limits are obtainable. Cases are given below, *e.g.*, in BaD.

For low atomic weights δ_1 is always a small quantity and except for orders where $m = 1$ or 2 , the alteration in wave number is small. For the present purpose which is to obtain proof of the existence of the displacements here indicated, no evidence can be admitted in which the change in wave number produced by a displacement $\frac{1}{2}\delta_1$, is comparable with the possible error of observation. The evidence, therefore, is of

greatest weight when derived from the spectra of elements of high atomic weight, or from cases in which the displacements are due to multiples of Δ .

It is possible for a line to be simultaneously displaced to right and left, as for instance $\text{CaS}_1(2)$ given above. Such lines exist, but since there is a very considerable scope for adjustment of values by a proper choice of say x and y in $(x\delta) X (y\delta)$, and specially so in y when $m > 2$, such cases cannot be considered as established unless δ is very large, or the Δ enter only, or unless there is independent evidence by the existence of intermediate steps.

When these collaterals were first found it was noticed that in general a positive displacement seemed in the majority of cases to increase the intensity of the lines, and a negative to decrease it. This is clear when the displacements considered are those from the 1st to the 2nd set of a doublet series where the displacement is a negative one and there is always a decrease in intensity. It is also evident in the satellites of the D series. Apparently, as will be shown, the typical line of the series is the satellite. The strong line is a positive collateral of this and always shows a great increase of intensity. Although these facts are obvious the connection was not recognised, until the relation showed itself first in a series of collaterals. It is, I think, safe to say that a positive displacement produces a tendency to increase of intensity; there may be other causes acting so as sometimes to mask the effect, but in general, where the rule appears to be broken, the suggested displacements should be regarded with some doubt. In so far as I have used this rule in the following, the results are biased and of course the evidence for the rule to that extent weakened.

It would be possible to give here long lists of collaterals. As, however, the present communication has reference chiefly to the discovery of general laws as a necessary preliminary to the more thorough examination of special spectra, it will be sufficient to refer for evidence to the cases which arise in the succeeding discussion. This seems, however, a natural place to refer to certain cases discussed in Parts I. and II., where unexpected deviations occurred between the calculated and observed position of a line in the middle of a series in which for the other lines the agreement was especially good. As special instances, the cases of $\text{TlS}_1(4)$ and $\text{CaS}_1(5)$ [II., p. 39] may be taken. The suggestion that $\text{TlS}_1(4)$ may be due to a transcription error is not valid, and was occasioned by an oversight in confounding $d\lambda$ with dn . If the normal line be denoted by $\text{TlS}_1(4)$, the observed is the collateral $\text{TlS}_1(4)(15\delta_2)$ giving $O-C = -\cdot 01$ in place of $-1\cdot 21$. Similarly, the observed Ca line is $\text{CaS}_1(5)(-6\Delta_2)$ with $O-C = -\cdot 03$ in place of $\cdot 61$. There are many examples of such sudden jumps which are certainly not due to errors of observation. Several instances will be found below in the D series.

The Diffuse Series.

To the question what is the positive criterion of a Diffuse series no clear answer up to the present has been given. We find in general three sets of series associated together. Two of these have the same limits, the other a limit peculiar to itself.

The latter is the Principal series, and the difference between the wave numbers of its first line and of its limit gives the limit of the other two. Of the other two series, one shows a Zeeman effect of the same nature as that in the Principal. This is called the Sharp series—or (by KAYSER and RUNGE) the 2nd associated series. The third series is called the Diffuse—or the 1st associated series. It has in fact a negative kind of criterion. The preceding definitions apply to the three series in all elements, including such elements as Li, He, and others which show singlet series. When doublets and triplets appear, we have a simple physical criterion for the Principal series in that it is that series in which the doublets or triplets converge with increasing order. This criterion can be applied even when the 1st line has not been observed. In certain elements the constant separations are shown between satellites. In these cases the series is certainly a D-series, at least in those recognised up to the present—but further knowledge may show that in certain cases such satellites may appear in other series.* If, passing beyond the mere physical appearance of the series or their visible arrangement in the spectrum, we attempt to represent their wave numbers by formulæ of the recognised types, we have further criteria for the Principal and Sharp, viz., that the 1st line of the Principal may also, very nearly at least, be calculated from the formula for the Sharp—or *vice versâ*—and that the denominators in their formulæ differ, roughly indeed but sufficiently closely for use as a criterion, by a number not far from '5. But when an attempt is made to deal in the same way with a line of the diffuse series, no general type of formula has, at least as yet, been found. In the alkali metals, as was seen in [I.] all the D-series take a positive value for α —in other words, the fractional parts of the denominators decrease with increasing order, and the general conclusion might be drawn that this was a common feature of all diffuse series. But the opposite occurs in the triplet spectra of the 2nd group of elements, whilst a similar rule of a positive value of α recurs in the 3rd group. This suggests that the series giving doublets have α positive and triplets α negative, but this is contradicted by the triplet series of O, S and Se, which behave in the same way as the doublets of Groups 1 and 3. The question naturally arises, is there a typical D-sequence with α positive, and the diffuse series in the 2nd group do not really belong to this type, or is there no actual D-sequence, *i.e.*, no regular type of formula to which the D-series conform. The difficulty of finding formulæ to accurately represent any particular D-series would point to the latter supposition, a supposition also which is strengthened when we study comparatively the series of numerical values of the denominators found directly from observations as is done below. In the case of the alkalis the formulæ given in [I.] (as well as those in $1/m^2$) do not reproduce well the high orders and are probably only within the limits of error because the lines are so diffuse that the observation errors are very large. In fact one of the few excessive deviations found in [I.] was that of NaD (6), in which it is

* *E.g.*, in ScS., see Appendix I.

not probable that the error is one of observation. In Group 2 the Zn sub-group can be reproduced fairly well with a formula in $\alpha/(2m-1)$ in which α is negative. Mg can also be reproduced within error limits by a formula of the same kind, but it is impossible to do so for Ca, and Sr and Ba require additional terms in $1/m^2$. In Group 3 Al is quite intractable, and if really depending on a formula, appears to require complicated algebraic or circular functions. In and Tl also are not amenable to formulæ in α/m only or $\alpha/m + \beta/m^2$. Nevertheless, the general build of the series is so similar to that of the others that it would seem probable that the wave numbers should also be of the form $S(\infty) - N/(m+d_m)^2$. If so it is possible to calculate d_m from the observations and a comparative study may throw some light on the origin of the different lines. The attempt to deal with these series from the formulæ point of view, however, brought out the fact that the satellites are related to the strong lines in a similar way to that in which the Principal line doublets are, viz., by a constant difference in the denominators and that their differences probably depend on multiples of the "oun," as is the case in the Principal series. As the evidence depends also on a comparison of the numerical values of d_m , this point will also be considered now.

The actual values of d_m will depend on the accuracy of the value $S(\infty)$ (or $D(\infty)$) of the limit. In the calculations below the most probable value has been used (see note under each element) and the true value has been taken to be that $+\xi$. In order to be free from mental bias these have been in general taken to be the same as $S(\infty)$, which involves the theorem that $D(\infty) = S(\infty)$. But of this little doubt can be felt. The true values of d_m can then be given in the form $d_m + k\xi$ where k is small. For high orders of m , k is comparatively large and can only be used when ξ is very small. It is however generally the case that errors made in this way are only a fraction of the observational errors.

As in the normal type where there are no satellites $VD_1 = VD_2 = VD_3$, and where there are satellites $VD_{12} = VD_{21}$, $VD_{13} = VD_{31}$, it is only necessary to tabulate the values of d_m for the case of VD_1 or VD_{11} , VD_{12} , VD_{13} respectively. When this is done certain regularities are clearly apparent, which can be made more exact by allowing small observational errors and giving a small permissible value to ξ . It would cumber the space at disposal to give both sets of values, especially as it is possible to easily indicate the differences on the one set of tables. Table II. then gives the values of D_m with the modified value of ξ , with the maximum errors attached in the usual way in (), and the calculated value given as a correction to the selected value. Thus for NaD (3), $D(3) = 3.986626(133) - 289\xi - 104$, 3.986626 is the selected value, 133 possible change in last three digits in this, -289 is change for $\xi = +1$, and the observed value is 104 less than the selected. The values of the errors of observed wave-length over calculated (O-C), and of possible observed errors (O) are given in each case on the right. The tables for the different elements are collected together and discussion of each is given later when considering the ordinal relations of the denominators.

TABLE II.

Na.

$$\Delta = 743. \quad \delta = 19.17.$$

K.

$$\Delta = 2939. \quad \delta = 55.45.$$

| | D. | O-C. | O. |
|------|---|------|-----|
| S. | $2.988656(36) - 121\xi$ $2030 = 3\Delta - 200$ | | |
| K.R. | $3.986626(133) - 289\xi - 104$ 4Δ | .02 | .03 |
| „ | $4.983654(452) - 565\xi + 35$ 4Δ | -.01 | .2 |
| „ | $5.980682(2248) - 977\xi - 81$ 17Δ | .02 | .5 |
| Z. | $6.968051(?) - 1545\xi + 23$ -28Δ | 0 | ? |
| „ | $7.988855 - 2329\xi - 528$ | | |
| „ | $8.988857 - 3324\xi - 850$ | | |
| „ | $9.98886 - 456\xi - 520$ | | |
| „ | $10.990 - 6.1\xi$ | | |
| „ | $11.992 - 7.9\xi$ | | |
| „ | $12.999 - 10.1\xi$ | | |
| „ | $13.986 - 12.6\xi$ | | |
| „ | $14.951 - 15\xi$ | | |

| | D. | O-C. | O. |
|------|---|------|-----|
| P. | $2.853302(38) - 106\xi$ $57936 = 20\Delta - 844$ | | |
| S. | $3.795366(224) - 249\xi + 167$ 9Δ | -.30 | .4 |
| K.R. | $4.768915(74) - 494\xi - 61$ 5Δ | .04 | .05 |
| „ | $5.754220(452) - 869\xi + 348$ 3Δ | -.11 | .15 |
| „ | $6.745786(1050) - 1400\xi + 381$ 2Δ | -.07 | .2 |
| „ | $7.739527(8462) - 2115\xi + 867$ | -.10 | 1.0 |
| S.* | 8.723519 | | |
| L.D. | 9.731179 | | |
| L.D. | 10.686 ? D line | | |

* S. gives $\nu = 61.25$; L.D. give 59.15 ; both give $D_2(8)$ the same. If we take this as correct and make $\nu = 57.87$, the denominator = 8.733756 . L.D.'s value = 8.729879 .

Na. $NaP(\infty)$ is given in [I.] = 41446.76 ± 1.69 , but WOOD's measurements of the high orders require a value about 1.48 larger, say, close to 41448.24 . Also FABRY and BUISSON's interferometer measure of $NaP(1)$ give, when referred to HARTMANN's R scale, $n = 16972.85$. Whence

$$VP(1) = 41448.24 - 16972.85 = 24475.39$$

and this should be $D(\infty)$ and $S(\infty)$. Further, $S(\infty)$ is given in [I.] as 24472.11 ± 3.84 and ZICKENDRAHT's measures of high order require about 3 or 4 more, or, say, 3.5 , which is within allowable limits. This would give $S(\infty) = D(\infty) = 24475.61$. Thirdly, $D(\infty)$, calculated from $m = 3, 4, 5$, gives 24475.20 . ZICKENDRAHT's measures, however, if exact, require about 2 larger. The three combined appear to point to a value close to 24475.40 , and this was taken for calculation. In the modified table above, it was found better to take $D(\infty)$ about 1 larger, in the direction of ZICKENDRAHT's results, and the table is therefore based on 24476.40 . For $NaD(6)$ ZICKENDRAHT, as well as K.R., gives an abnormally great separation. LEHMANN's value of $D_1(2)$ gives 243 greater, making 1st ordinal difference = 3Δ . K.R.'s value of $D(6)$ gives 6.965755 .

K. $KP_1(\infty)$ from [I.] = 35006.21 ± 1.55 and agrees well with BEVAN's measures of high orders, possibly slightly less. For $P_1(1)$ K.R. give $n = 13041.77$ and S 13042.96 . These, then, give for $D(\infty) = S(\infty) = 21964.44$ or less (K.R.) and 21963.25 , or less, (S.). The value 21964 has been taken

TABLE II. (continued).

Rb.

$$\Delta = 12935. \quad \delta = 263.77.$$

| | D. | O - C. | O. |
|----------|--|--------|-----|
| RAN. | $2.766216 - 96\xi$ 60669 = 230δ | | |
| S. | $3.705547 - 232\xi + 0$ 83δ | .00 | ? |
| " | $4.683718 (234) - 468\xi - 26$ 38δ | .05 | .20 |
| K.R. | $5.673688 (382) - 833\xi + 22$ 19δ | -.00 | .15 |
| " | $6.668673 (676) - 1352\xi - 118$ 15δ | .01 | .15 |
| R. or S. | $7.664713 - 2053\xi - 68$ 14δ | 0 | ? |
| S. | $8.661017 - 2963\xi - 70$ | 0 | ? |
| " | $9.661017 - 4114\xi + 391$ | 0 | |
| " | $10.6428 - 55\xi$ | | |
| " | $11.6464 - 72\xi$ | | |
| " | $12.635 - 9\xi$ | | |

$RbP_1(\infty) = 33687.50 \pm 2$ [I.], and probably greater. BEVAN'S observations show slightly larger, say, about .5, *i.e.*, $P(\infty) = 33688$. Using SAUNDERS' for $P_1(1)$, $VP(1) = 20871.29 = D(\infty)$.

According to SAUNDERS, RbD shows satellites for $m = 3$ and 4, giving $D_{11}(3) - D_{12}(3) = 2.63$ and $D_{11}(4) - D_{12}(4) = 2.02$ with uncertainties of 1. These give differences in the denominators respectively of 610 and 946, and $9\delta_1 = 593$, $14\delta_1 = 923$.

Cs.

$$\Delta = 32551. \quad \delta = 638.22.$$

| | D_{11} . | D_{12} . | O - C. | O. | O - C. | O. |
|----|--|--|--------|----|--------|----|
| P. | $2.554329 (228) - 76\xi - 43$ 30δ | $.546989 (226) - 97$ 46δ_1 | -.5 | 3 | -1.3 | 3 |
| " | $3.535183 (200) - 201\xi + 40$ 10δ_1 | $.526567 (200) + 9$ 54δ_1 | .2 | 1 | .0 | 1 |
| S. | $4.533588 (160) - 424\xi + 1$ 3δ_1 | $.524635 - 161$ 14δ | .00 | .5 | .5 | ? |
| " | $5.533110 (400) - 768\xi + 22$ 3δ_1 | $.524175 - 26$ 14δ | | | | |
| R. | $6.532631 - 1264\xi + 77$ 14δ | $.523696 - 428$ 14δ | | | | |
| " | $7.532631 - 1945\xi - 158$ | | | | | |
| " | $8.532631 - 2826\xi + 56$ | | | | | |
| " | $9.525411 - 3975\xi$ | | | | | |
| " | $10.52533 - 530\xi$ | | | | | |
| " | $11.5326 - 70\xi + 11$ | | | | | |

TABLE II. (continued).

Since the publication of [I.] RANDALL* has measured $P(1)$ with considerable accuracy. This, with $P(2, 3)$, gives $P_1(\infty) = 31401.78$, and RANDALL'S value for $P_1(1)$ gives $VP(1) = 19673.12$. BEVAN'S observations show $P_1(\infty)$ about 2 larger. Probably, however, this value for $VP(1)$ is close to the true value for $D(\infty)$, and the calculations are based on $D(\infty) = 19673.00$.

For $D_1(3)$ LEHMANN gives denominators 548 larger for D_{11} and 548 less for D_{12} . If we allow S. twice the weight of L. the value of O - C would come out about zero.

Cu.

$$\Delta = 7311. \quad \delta = 146.22.$$

| D_{11} | D_{12} | O - C. | O. | O - C. | O. |
|--|--------------------------------|--------|-----|--------|-----|
| $2.979076(43) - 120\xi - 6$ 34 δ | $23\delta_1 \cdot 978272 + 4$ | .01 | .10 | -.01 | .05 |
| $3.984047(173) - 288\xi + 24$ 10 δ | $27\delta_1 \cdot 983060 + 30$ | -.01 | .10 | -.01 | .20 |
| $4.985509(?) - 565\xi + 35$ | | -.01 | ? | | |

$D(\infty) = 31515.48$ found from K.R.'s value for $D(2, 3, 4)$.

Ag.

$$\Delta = 27791. \quad \delta = 421.07.$$

| D_{11} | D_{12} | O - C. | O. | O - C. | O. |
|---|---------------------------------------|--------|------|--------|-----|
| $2.979583(19) - 120\xi + 3$ 41 δ_1 | $23\delta_1 \cdot 977150(19) + 12$ | -.01 | .05 | -.03 | .05 |
| $3.983898(1967) - 288\xi + 23$ 32 δ_1 | $10\delta_1 \dagger 982891(175) - 27$ | -.01 | 1.00 | .01 | |
| $4.987280(7776) - 565\xi - 2$ 9 δ_1 | $15\delta_1 \dagger 985701(2170)$ | .00 | 2.00 | .00 | |
| $5.988130(3720) - 979\xi + 46$ | | .00 | .50 | | |

† Calculated from $D_2 - \nu$.

$D(\infty)$ found from first three by formula = 30644.66, modified to 30644.76.

The limit uncertain, see special discussion (p. 403).

The observation errors after the first are so large that the satellite differences might be also $23\delta_1$, or larger, as in Cu.

* "Zur Kenntnis ultraroter Linienspektra," 'Ann. d. Phys.' (IV.), 33, p. 743.

TABLE II. (continued).

Mg.

$$\Delta_1 = 854. \quad \Delta_2 = 413. \quad \delta = 21.48.$$

| | D. | O - C. | O. |
|------|--|--------|-----|
| P. | $1.822169 - 27.5\xi + 12$ | -1 | 1.5 |
| K.R. | $2.828774 (20) - 103\xi - 12$ $16\Delta_2$ | .02 | .03 |
| | $3.831255 (79) - 256\xi + 59$ $6\Delta_2$ | -.02 | .03 |
| * | $4.832494 (190) - 514\xi + 61$ $3\Delta_2$ | -.01 | .03 |
| | $5.833320 (1808) - 904\xi - 24$ $2\Delta_2$ | .00 | .15 |
| † | $6.833320 (4210) - 1452\xi - 583$ | .02 | .20 |

* Calculated from $D_{21} - \nu_1$.

† The observed value gives $\nu_1 = 42.87$ in place of the normal value 40.92 . If this be corrected to 40.92 , giving equal weights to D_2, D_3 , the value would be 6.833809 .

$D(\infty) = S(\infty) = 39752.83 \pm 2.73$, as given in [II.], from the formula in $1/m^2$. This is modified in the above to 39751.08 .

Ca.

$$\Delta_1 = 2791. \quad \Delta_2 = 1369. \quad \delta = 58.14.$$

| D_{11} . | D_{12} . | D_{13} . | O - C. | O. | O - C. | O. | O - C. | O. |
|---|------------------------------------|----------------------------------|--------|-----|--------|-----|--------|-----|
| $1.947172 (8) - 33\xi - 4$ | $13\delta \cdot 946417 (25) + 5$ | $8\delta \cdot 945952 (25) + 20$ | .5 | 1.0 | -.6 | 2.0 | -2.4 | 3 |
| $3.082696 (20) - 133\xi + 14$ $99\Delta_2$ | $13\delta \cdot 081941 (20) + 11$ | $8\delta \cdot 081476 (20) - 14$ | -.02 | .03 | -.01 | .03 | .02 | .03 |
| $4.091707 (104) - 312\xi + 17$ 155δ | $14\delta \cdot 090893 (104) - 17$ | $*.090428 - 21$ | 0 | .05 | 0 | .05 | .01 | .05 |
| $\dagger 5.091707 (538) - 598\xi + 326$ 0 | | | -.06 | .10 | | | | |
| $\dagger 6.091707 (4856) - 1012\xi - 1400$ 0 | | | .14 | .50 | | | | |
| $\dagger 7.091707 (7732) - 1546\xi + 161$ 0 | | | -.02 | .50 | | | | |

* Calculated from D_{22} and D_{31} , treating each as of equal value.

† Collaterals (see text). The values calculated direct from the observations are respectively 5.082736 , 6.056500 , 6.976528 .

$D(\infty) = 33981.85$, being 33983.45 ± 5.8 , as given for $S(\infty)$ in [II.], with $1/m^2$ modified by putting $\xi = -1.6$.

TABLE II. (continued).

Sr.

$$\Delta_1 = 11835. \quad \Delta_2 = 5533. \quad \delta = 277.89.$$

| D ₁₁ . | D ₁₂ . | D ₁₃ . | O - C. | O. | O - C. | O. | O - C. | O. |
|-------------------------------------|----------------------------|------------------------|--------|-----|--------|-----|--------|-----|
| 1.993184 (7) - 36ξ + 1 653δ | 13δ · 989572 (8) - 7 | 8δ * · 987349 + 45 | - .3 | 1.5 | 1.7 | 2.0 | ? | ? |
| 3.174741 (17) - 146ξ + 15 84δ | 12δ · 171407 (17) - 7 | 8δ · 169184 (29) + 15 | - .02 | .03 | .01 | .03 | - .02 | .05 |
| 4.198084 (101) - 337ξ + 41 19δ | 15δ · 193916 (100) - 82 | 8δ · 191693 (?) + 597 | - .02 | .05 | .04 | .05 | .30 | ? |
| 5.203364 (963) - 642ξ + 112 2δ | 15δ † · 199196 (482) + 300 | 8δ † · 196973 (?) - 84 | - .02 | .20 | - .06 | ? | | |
| 6.203919 (2539) - 1088ξ - 40 0 | 15δ ‡ · 199751 (?) + 210 | | .00 | .30 | - .02 | ? | | |
| 7.203919 (2838) - 1702ξ - 1819 0 | | | .12 | .20 | | | | |
| 8.203919 (20174) - 2522ξ + 5971 | | | - .3 | 1.0 | | | | |

* Calculated from D₃₁ - ν₁ - ν₂. The difference might be 7³/₄δ = 31δ₁.

† Calculated from D₂₁ - ν₁ and D₂₂ - ν₁.

‡ Calculated from D₂₁ - ν₁.

D(∞) = 31027.25, being 31027.65 ± 4, as given for S(∞) in [II.], with 1/m², modified by putting ξ = -.4.

Ba.

$$\Delta_1 = 29328. \quad \Delta_2 = 11976. \quad \delta = 683.2.$$

| D ₁₁ . | D ₁₂ . | D ₁₃ . | O - C. | O. | O - C. | O. | O - C. | O. |
|------------------------------------|--------------------------|---|--------|-----|--------|-----|--------|-----|
| 3.114613 (12) - 137ξ - 11 64δ | 14δ · 105049 (20) + 19 | 11δ · 093194 (20) - 11 1.825551* } 2.086655 } | .02 | .03 | - .04 | .05 | .02 | .05 |
| 4.158338 (812) - 325ξ + 24 -14δ | 10δ · 151506 (325) - 154 | 29δ · 131694 (160) + 101 | - .01 | .50 | .09 | .20 | - .06 | .10 |
| 5.148774 - 49 | | | ? | ? | | | | |
| 6.1517 | | | | | | | | |
| 7.0414 | | | | | | | | |

* Possibly not BaD (see text).

D(∞) = 28610.63, being 28642.63 ± ?, as given for S(∞) in [II.], with 1/m, modified by ξ = -.32 as explained in text, p. 358.

TABLE II. (continued).

Ra.

$$\Delta_1 = 92658. \quad \delta = 1853.16.$$

| D ₁₁ . | D ₁₂ . | D ₁₃ . | O - C. | | |
|--|-------------------------------|-------------------|--------|-------|-----|
| 4.065042 - 306ξ 35δ ₁ | 2δ ₁ ·064116 + 10 | 2δ ·060410 - 46 | ·00 | - ·01 | ·05 |
| 5.081257 - 598ξ + 26 21δ ₁ | 2δ ₁ ·080331 + 115 | | - ·01 | - ·05 | |
| 6.090986 - 1028ξ + 22 | | | ·00 | | |

$D(\infty) = 22760.19$, being 22760.09 , as given for $D(\infty)$ in [II.], modified by $\xi = .1$.

The numbers are calculated from the problematic data given in [II., p. 65].

Zn.

$$\Delta_1 = 7204.42. \quad \Delta_2 = 3486.20. \quad \delta = 154.93.$$

| D ₁₁ . | D ₁₂ . | D ₁₃ . | O - C. | O. | O - C. | O. | O - C. | O. |
|--|-------------------------------------|------------------------------------|--------|-------------------|--------|-----|--------|-----|
| 2.905892 (28) - 112ξ - 20 7δ ₆ | 15δ ₁ ·905311 (49) + 36 | 9δ ₁ ·904963 (100) - 15 | ·02 | ·03 | - ·03 | ·05 | 0 | ·10 |
| 3.907519 (108) - 272ξ + 6 6δ ₆ | 13δ ₁ ·907015 (108) + 54 | 10δ ₁ ·906627 (?) + 43 | - ·00 | ·03 | - ·01 | ·03 | - ·01 | |
| 4.908913 (404) - 539ξ - 8 4δ ₆ | | | ·00 | ·05 | | | | |
| 5.909843 (2961) - 940ξ - 40 *6.909593 (4068) *7.910072 (11320) | | | ·00 | ·20 ·20 ·30 | | | | |

* Collaterals (see text).

$D(\infty) = 42874.17$ being $S(\infty) = 42876.42 - 1.08$, as given in [II.], modified by $\xi = -2.25$.

D_{12} , D_{13} are calculated from the more accurate D_{21} , D_{22} by the use of the exact value of $\nu_1 = 388.905$.

TABLE II. (continued).

Cd.

$$\Delta_1 = 23105.56. \quad \Delta_2 = 10368.54. \quad \delta = 455.28.$$

| D ₁₁ . | D ₁₂ . | D ₁₃ . | O - C. | O. | O - C. | O. | O - C. | O. |
|--|--------------------------------------|-------------------------------------|--------|-----|--------|-----|--------|-----|
| 2.902039 (28) - 111ξ - 13 75δ ₁ | 18δ ₁ · 899990 (44) + 7 | 11δ ₁ · 898748 (83) + 15 | ·01 | ·03 | - ·01 | ·05 | - ·02 | ·10 |
| 3.910576 (91) - 272ξ - 11 31δ ₁ | 19δ ₁ · 908413 (630) - 22 | 15δ ₁ · 906706 (?) + 2 | ·00 | ·03 | ·00 | ·20 | 0 | ? |
| 4.914104 (216) - 541ξ - 19 12δ ₁ | 19δ ₁ · 911941 (708) + 31 | 15δ ₁ | ·00 | ·03 | ·00 | ·10 | | |
| 5.915470 (2656) - 942ξ - 29 11δ | | | ·00 | ·20 | | | | |
| 6.920598 (6648) - 1511ξ - 60 | | | ·00 | ·30 | | | | |

$$D(\infty) = 40710.85 \text{ being } S(\infty) = 40710.60 + \frac{2.15}{.73}, \text{ as given in [II.], modified by } \xi = .25.$$

Eu.

$$\Delta_1 = 51223. \quad \Delta_2 = 18329. \quad \delta = 833.04.$$

| D ₁₁ . | D ₁₂ . | D ₁₃ . | O - C. | | |
|--|--------------------------------|--------------------------------|--------|-----|-------|
| 2.930707 - 114ξ 57δ ₁ | 29δ ₁ · 924667 - 25 | 33δ ₁ · 917794 + 26 | 0 | ·03 | - ·03 |
| 3.942578 - 279ξ - 5 20δ ₁ | | | 0 | | |
| 4.946742 - 552ξ + 17 13δ ₁ | | | 0 | | |
| 5.949450 - 960ξ + 94 | | | 0 | | |

$$D(\infty) = 40363.19 \text{ being } S(\infty) \text{ in [II., p. 73]. No estimated possible errors given.}$$

TABLE II. (continued).

Hg.

$$\Delta_1 = 87814.99. \quad \Delta_2 = 30002.3. \quad \delta = 1451.49.$$

| D ₁₁ . | D ₁₂ . | D ₁₃ . | D ₁₄ . | O - C. | O. | O - C. | O. | O - C. | O. | O - C. | O. | O - C. | O. |
|---|-------------------------------------|------------------------------------|-------------------------------------|--------|-----|--------|-----|--------|-----|--------|-----|--------|-----|
| 2.932562 (25) - 115ξ - 5 28δ ₁ | 11δ ₁ .928571 (38) + 6 | 19δ ₁ .921671 (38) - 9 | δ ₁ .921314 + 8 | .00 | .03 | -.01 | .05 | .01 | .05 | -.01 | .05 | -.01 | .05 |
| 3.942723 (151) - 279ξ + 37 9δ ₁ | 17δ ₁ *.936554 (197) + 5 | 18δ ₁ .930022 (611) + 7 | 15δ ₁ .924579 (418) + 52 | -.01 | .05 | .00 | .20 | .00 | .20 | -.01 | .20 | -.01 | .15 |
| 4.945989 (1396) - 552ξ - 36 6δ ₁ | 16δ ₁ .940183 - 12 | 17δ ₁ .934014 - 105 | 27δ ₁ .924216 - 57 | .00 | .20 | .00 | ? | .01 | ? | .00 | ? | .00 | ? |
| 5.948130 (?) - 960ξ + 89 6δ ₁ | 22δ ₁ .940147 + 85 | 51δ ₁ | .921641 + 75 | .00 | ? | .00 | ? | .00 | ? | .00 | ? | .00 | ? |
| 6.950307 7.948774 8.956716 } 18δ ₁ (?) | - 132 | | | | | | | | | | | | |
| 12.956 | | | | | | | | | | | | | |
| 15.949 | | | | | | | | | | | | | |

* Calculated from D₂₁.

$$D(\infty) = 40140.35, \text{ being } S(\infty) = 40139.55 + 5.41 - .99, \text{ as given in [II.], modified by } \xi = .8.$$

TABLE II. (continued).

Al.

$$\Delta = 1754. \quad \delta = 26.57.$$

| D ₁₁ . | | D ₁₂ . | O - C. | O. | O - C. | O. |
|-------------------------------|-----|-------------------|--------|-----|--------|-----|
| 2.631287 (25) - 83ξ + 0 | 4δ | .631181 (25) + 12 | .00 | .03 | -.01 | .03 |
| 117Δ | | | | | | |
| 3.426069 (82) - 183ξ - 5 | 30δ | .425272 (82) - 8 | .00 | .03 | .00 | .03 |
| 94Δ | | | | | | |
| 4.261194 (200) - 353ξ + 20 | 52δ | .259812 (200) + 2 | .00 | .03 | .00 | .03 |
| 54Δ | | | | | | |
| 5.166498 (620) - 629ξ - 130 | | | .01 | .05 | | |
| 29Δ | | | | | | |
| 6.115632 (2088) - 1044ξ + 160 | | | .00 | .10 | | |
| 16Δ | | | | | | |
| 7.087568 (3431) - 1626ξ + 666 | | | -.02 | .10 | | |
| 7Δ | | | | | | |
| 8.0753 + 400 | | | | .2 | | |
| 9.0604 | | | | .2 | | |
| 10.0523 | | | | .2 | | |

D(∞) = 48164.12 being S(∞) = 48161.46 ± 2.49, as given in [II.], modified by ξ = 2.66.

In.

$$\Delta = 37684. \quad \delta = 477.01.$$

| D ₁₁ . | | D ₁₂ . | O - C. | O. | O - C. | O. |
|-----------------------------|-----|---------------------|--------|-----|--------|-----|
| 2.823978 (48) - 102ξ + 10 | 5δ | .821593 (48) - 10 | -.01 | .05 | .01 | .05 |
| 37δ | | 58δ | | | | |
| 3.806329 (167) - 251ξ - 76 | 26δ | .793927 (167) - 154 | .02 | .05 | .04 | .05 |
| 62δ | | 62δ | | | | |
| 4.776755 (392) - 497ξ - 20 | 26δ | .764353 (784) - 287 | .00 | .05 | .03 | .10 |
| 44δ | | 50δ | | | | |
| 5.755767 (2954) - 869ξ - 63 | 32δ | .740503 (7343) - 98 | .00 | .20 | .00 | .50 |
| | | 50δ | | | | |
| 6.696300 (4791) - 1369ξ | | *.716653 - 179 | | .20 | .08 | .30 |
| 7. | | *.715387 | | | | .30 |
| 8. | | *.717621 | | | | .30 |
| 9. | | *.717556 | | | | .30 |
| 10. | | | | | | .30 |
| 11. | | | | | | ? |

* Collaterals (2δ₁) D₂ (m).

D(∞) = 44454.76 ± 2.48 being S(∞) of [II.]

TABLE II. (continued).

Tl.

$$\Delta = 134154. \quad \delta = 1507.34.$$

| D_{11} . | | D_{12} . | O - C. | O. | O - C. | O. |
|--|----------------|-----------------------|--------|-----|--------|-----|
| $2 \cdot 897392$ | } $24\delta_1$ | $* \cdot 888344$ | - .01 | .03 | .02 | .03 |
| $* 2 \cdot 899520 (80) - 111\xi + 10$ | | $* \cdot 890476 - 16$ | | | | |
| $2\delta_1$ | | $5\delta_1$ | | | | |
| $3 \cdot 898764 (89) - 270\xi - 30$ | $27\delta_1$ | $* \cdot 888590 + 53$ | .01 | .03 | - .02 | .03 |
| $2\delta_1$ | | $3\delta_1$ | | | | |
| $4 \cdot 898010 (213) - 535\xi - 26$ | $28\delta_1$ | $\cdot 887459 + 53$ | .00 | .03 | .00 | .03 |
| $3\delta_1$ | | $3\delta_1$ | | | | |
| $5 \cdot 896880 (414) - 935\xi + 1$ | $28\delta_1$ | $\cdot 886329 - 116$ | .00 | .03 | .01 | .03 |
| $3\delta_1$ | | $3\delta_1$ | | | | |
| $6 \cdot 895750 (2287) - 1495\xi - 220$ | $28\delta_1$ | $\cdot 885199 + 39$ | .01 | .10 | .00 | .10 |
| $3\delta_1$ | | | | | | |
| $7 \cdot 894620 (3431) - 2242\xi - 1197$ | | | .03 | .10 | | |
| $8 \cdot 894620 (5134) - 3209\xi + 301$ | | | .00 | .10 | | |
| $9 \cdot 894620 (7067) - 4417\xi - 591$ | | | .01 | .10 | | |
| $10 \cdot 8946 + 33$ | | | - .03 | .20 | | |
| $11 \cdot 8946 + 31$ | | | - .02 | .20 | | |
| $12 \cdot 8946 + 70$ | | | - .04 | .30 | | |
| $13 \cdot 8946 + 278$ | | | - .14 | .30 | | |
| $14 \cdot 8946 + 406$ | | | - .16 | .30 | | |

* Collaterals (see text).

 $D(\infty) = 41470.53 \pm 1.72$ being $S(\infty)$ of [II.] modified by $\xi = .3$.

O.

$$\Delta_1 = 172. \quad \Delta_2 = 95. \quad \delta = 9.33.$$

| D''' . | O - C. | O. | D'' . | O - C. | O. |
|---------------------------------------|--------|------|---------------------------------------|--------|------|
| $2 \cdot 972467 (40) - 120\xi + 16$ | - .12 | .3 | $2 \cdot 980383 (93) - 121\xi - 3$ | .03 | 1.00 |
| $34\Delta_1$ | | | $9\Delta_1$ | | |
| $3 \cdot 966621 (14) - 284\xi - 12$ | .015 | .018 | $3 \cdot 978835 (72) - 287\xi + 7$ | - .026 | .26 |
| $14\Delta_1$ | | | $9\Delta_1$ | | |
| $4 \cdot 964213 (18) - 558\xi + 15$ | - .008 | .01 | $4 \cdot 977287 (33) - 562\xi + 28$ | - .017 | .02 |
| $8\Delta_1$ | | | $3\Delta_1$ | | |
| $5 \cdot 962837 (38) - 966\xi + 20$ | - .005 | .01 | $5 \cdot 976771 (68) - 974\xi - 33$ | .010 | .02 |
| $5\Delta_1$ | | | Δ_1 | | |
| $6 \cdot 961977 (67) - 1538\xi - 15$ | .005 | .01 | $6 \cdot 976599 (215) - 1547\xi + 38$ | - .007 | .04 |
| $2\Delta_1$ | | | $7 \cdot 986756 (626) - 2321\xi$ | | .07 |
| $7 \cdot 961633 (309) - 2301\xi + 20$ | - .001 | .03 | $8 \cdot 985948 (6610) - 3305\xi$ | | .5 |
| $2\Delta_1$ | | | | | |
| $8 \cdot 961285 (951) - 3281\xi - 63$ | .003 | .06 | $9 \cdot 976599 (?) - 4523\xi + 1042$ | - .06 | ? |
| $9 \cdot 965800 (?) - 4521\xi$ | | | | | |

 $D'''(\infty) = 23204.1.$
 $D''(\infty) = 21204.2.$
The observed D'' corrected to give $\nu = .72$, treating the observed line as the mean of the doublet.

TABLE II. (continued).

S.

$$\Delta_1 = 1044. \quad \Delta_2 = 651.7. \quad \delta = 37.28.$$

| | O - C. | O. |
|---|--------|-----|
| $4.553453(47) - 430\xi + 7$ | - .01 | .05 |
| $5.544330(21) - 776\xi - 7$ $14\Delta_2$ | 0 | .01 |
| $6.539110(38) - 1273\xi - 29$ $5\Delta_1$ | .007 | .01 |
| $7.535978(194) - 1944\xi + 173$ $3\Delta_1$ | - .02 | .03 |
| $8.533890(396) - 2828\xi - 202$ $2\Delta_1$ | .02 | .04 |
| $9.529714(1141) - 3936\xi - 129$ $4\Delta_1$ | .01 | .08 |

$$D(\infty) = 20084.2.$$

Se.

$$\Delta_1 = 6407. \quad \Delta_2 = 2722. \quad \delta = 226.8.$$

Calculated from Observed Values.

| | |
|---------------------------|---------------|
| $4.629262(54) - 452\xi$ | *.626133(108) |
| $5.621963(56) - 810\xi$ | .622797 |
| $6.615643(105) - 1320\xi$ | .617055 |
| $7.601450(240) - 2002\xi$ | .608778 |
| $8.611058(728) - 2911\xi$ | |
| $9.592507(643) - 4024\xi$ | |
| $10.57831(270) - 540\xi$ | |

* Calculated from $D_{21} - D_{22}$.

$$D(\infty) = 19274.$$

Modified Table.

| | O - C. | O. | O - C. | O. | |
|--|-----------------|-------|--------|-------|-----|
| $4.629285 + 22$ 19δ $55\delta_1$ | $.626167 + 11$ | - .02 | .06 | - .01 | .09 |
| $5.624976 + 41$ 19δ $38\delta_1$ | $.622822 - 56$ | - .02 | .03 | .03 | ? |
| $6.620667 - 5$ 19δ $55\delta_1$ | $.617549 - 362$ | .00 | .03 | .10 | ? |
| $7.616358 + 156$ 19δ $55\delta_1$ | $.613240 - 531$ | - .02 | .04 | .09 | .09 |
| $8.612049 - 700$ 19δ | | .076 | .08 | | |
| $9.607740 + 91$ $\Delta_1 + \Delta_2$ | | - .00 | .05 | | |
| 10.59860 | | | .15 | | |

The Satellite Separations.—As the values of the satellite differences are practically independent of the exact value of $D(\infty)$, their consideration may be taken up at once and the details of the calculations respecting the tables postponed until the consideration of the order differences. An examination of the tables will show conclusively that these differences are multiples of the “oun.” Dealing first with the differences for the first lines, the following figures, contained implicitly in the tables, will show how closely this is the case. The nearest multiples of the oun are appended, as calculated from the first approximations of Table I. The possible errors are those of the D_{11} lines (except Zn).

| | | | | | |
|------------|--|---|------------|---|---|
| Cs | 7394 ± 228 | $46\delta_1 = 7340$ | Cd | $\left\{ \begin{array}{l} 2029 \pm 28 \\ 1234 \pm 44 \end{array} \right.$ | $\left\{ \begin{array}{l} 18\delta_1 = 2049 \\ 11\delta_1 = 1248 \end{array} \right.$ |
| Cu | 794 ± 43 | $22\delta_1 = 804$ | Eu | $\left\{ \begin{array}{l} 6065 \pm ? \\ 6822 \pm ? \end{array} \right.$ | $\left\{ \begin{array}{l} 29\delta_1 = 6040 \\ 33\delta_1 = 6873 \end{array} \right.$ |
| Ag | 2424 ± 19 | $23\delta_1 = 2422$ | Hg | $\left\{ \begin{array}{l} 3980 \pm 25 \\ 6909 \pm 38 \\ 346 \pm 38 \end{array} \right.$ | $\left\{ \begin{array}{l} 11\delta_1 = 3991 \\ 19\delta_1 = 6894 \\ \delta_1 = 363 \end{array} \right.$ |
| Ca | $\left\{ \begin{array}{l} 746 \pm 8 \\ 450 \pm 25 \end{array} \right.$ | $\left\{ \begin{array}{l} 51\delta_1 = 741 \\ 31\delta_1 = 451 \end{array} \right.$ | Al | 94 ± 35 | $14\delta_1 = 93$ |
| Sr | $\left\{ \begin{array}{l} 3620 \pm 7 \\ 2170 \pm ? \end{array} \right.$ | $\left\{ \begin{array}{l} 52\delta_1 = 3596 \\ 31\delta_1 = 2154 \end{array} \right.$ | In | 2405 ± 48 | $20\delta_1 = 2385$ |
| Ba | Not observed, as deduced below (p. 388), 15δ , 9δ , or $60\delta_1$, $36\delta_1$ | | Tl | 9048 ± 27 | $24\delta_1 = 9044$ |
| Zn | $\left\{ \begin{array}{l} 525 \pm 77 \\ 369 \pm 28 \end{array} \right.$ | $\left\{ \begin{array}{l} 15\delta_1 = 581 \\ 9\delta_1 = 350 \end{array} \right.$ | Se | 3129 ± 54 | $55\delta_1 = 3118$ |

The only case of “failure” is the first difference for Sr in which the estimated possible error is extremely small. If the possible error be the sum of those of each line, the value is 15 in place of 7, and if δ_1 be calculated from the most probable value of the oun it should be about $\frac{1}{90}$ greater, *i.e.*, $52\delta_1 = 3600$. It will be noted that where triplets enter, the two satellite differences, and consequently the two satellite separations, are extremely close to the ratio 5:3. This ratio seems to persist also in Hg where the separations are in reverse order, and we find a ratio of 3:5 in place of 5:3. The law for this ratio is in fact much more closely obeyed than the corresponding one for the ratio 2:1 for the triplet separations. It is therefore of great assistance in searching for the lines of F series whose limits are VD (2), and which consequently possess constant triplet separations in this ratio. Its explanation should be expected to throw some valuable light on the constitution of the atom. The general dependence of the differences on the small “oun” δ_1 should also be noted.

Passing now to the consideration of the satellite differences for orders beyond the first ($m > 2$), it is seen that they still depend on multiples of the oun, but different from those of the first order. In a large number of cases the multiples are the same

for different orders within limits of errors, especially in the doublets and differences of the second and third satellites. Thus we find Cs, 14δ ; Ca, 13δ , 8δ ; Sr, 12δ for $m = 3$ and 15δ for $m > 3$ for first separations, and 8δ for all orders in the second; Ba and Zn show too few for comparison (see discussion below); Cd, $19\delta_1$, $15\delta_1$; Hg is irregular, Al is anomalous; In 26δ , Tl, $27\delta_1$ for $m = 2$, and $28\delta_1$ for $m > 3$; Se, as amended later, shows $55\delta_1$ for $m = 4, 6, 7$, and $38\delta_1$ for $m = 5$, the lines for $m < 3$ being outside region of observation. The evidence points to a normal rule that the differences for the orders beyond the first in any spectrum are the same, but different from—in general greater than—that of the first.

The Order Differences.—The order differences change very considerably with a change in the value taken for the limit, *i.e.*, in the value given to ξ . No doubt with unlimited choice of ξ it would be possible to arrange a set of denominator differences all multiples of the own within error limits, for a series of values of ξ could be found making the first difference a multiple. Out of these one or two would probably give the second such a multiple. After the second the error limits as a rule come to be very large, in fact larger than half the own itself, except in case of very high atomic weight. No conclusions could be drawn from any such arrangement. But in the present cases the choice of ξ is bounded by very narrow limits, for the relation $D(\infty) = S(\infty)$ is supposed to hold, and, as a rule, the values of $S(\infty)$ are known with very considerable accuracy, and the possible limits of variation are known. They were given in [I.] and [II.]. Before proceeding to draw general conclusions from Table II., it will be well to consider in more detail the data for the different elements on which the table is based.

Na.

Although the readings for NaD are very inexact, the peculiarity of the large depression shown for $m = 6$, as well as the large recovery afterwards to mantissæ close to unity, must be real effects. It is of course possible that $\text{NaD}_1(6)$ is a collateral from the normal type. If $\text{D}_1(6)$ be calculated from $\text{D}_2(6) - \nu$, the mantissa becomes $\cdot 989054$, in other words, the D_2 line begins to show the rise to the large final value at $m = 6$, whilst D_1 does not do so until $m = 7$. The D_2 lines would seem to succumb to the disturbing effects sooner than the D_1 . It was pointed out in [I., p. 83] that in the Na the D series apparently belongs to the F type, in which the mantissa is $\cdot 998613$. It would almost seem that the peculiar rise shown is due to the fact that it reverts to this F sequence. Here, as we shall see in other cases, the values of the first members of these series appear to be subject to some kind of displacement which affects their (supposedly) normal relations to other lines. If now the first mantissa be supposed normally to be this $\cdot 998613$, it is 9691 above that in the modified table, and this is $13\Delta + 32$, thus completing the order differences as multiples of Δ . But in any case the data for Na are of small use for the present purpose, as the errors are so large, and Δ so small. The arrangement in the table

gives the values of $O-C$ least. If ξ be taken about $\cdot 6$, the order differences can run $3\Delta, 4\Delta, 4\Delta$ within error limits.

K.

It is seen that the numbers, with the exception as in other cases of the first difference, fall into multiples of Δ quite naturally without a change in $D(\infty)$, though possibly a small change in ξ might make the values of $O-C$ less. Δ is so large, that the theory of the dependence on multiples receives considerable support. The first also is close to 20Δ . This element is one in which the value given in the first discussion above for the oun is $362\cdot 68w^2$, which is presumably too large by $\cdot 8$ to $\cdot 9$. If it be $361\cdot 8$, Δ should be $\frac{1}{4\cdot 50}$ less and $= 2933$. This would scarcely effect the other intervals, but it would make the first one $= 20\Delta - 704$. Again there is a sudden fall (at $m = 8$). It doubtless corresponds to a real effect, for SAUNDERS as well as LIVEING and DEWAR make ν anomalous here. S. observes $\nu = 61\cdot 25$ and L.D. $59\cdot 15$, but both give $D_2(8)$ the same. If this be taken as correct and the normal $D_1(8)$ found from $D_2 - 57\cdot 87$, the mantissa is $\cdot 733756$, giving the same difference 2Δ . This shows that the D_2 set have not participated in the sudden fall—at least to the same degree as D_1 —a result analogous to what happens in Na.

Rb.

In Rb there is some doubt whether a satellite series exists. The question has already been discussed in [I., pp. 71, 86]. SAUNDERS has given for $D(3)$ lines whose wave numbers are $12883\cdot 93$, $12886\cdot 56$, and $13121\cdot 19$, with normal separations $237\cdot 26$, and satellite separations $2\cdot 63$. Also $D(4)$ is a doublet having a separation $235\cdot 52$, which certainly points to an unobserved satellite about $2\cdot 4 \pm \cdot 1$. But RANDALL'S observations for $D(2)$ show only a doublet of normal separation—that is clearly with no satellite. Moreover the F series, which depends on $D_{11}(2)$ and $D_{12}(2)$ for its limits, is a singlet series and not a double one. In the table the series is taken as if it were without a satellite, the reading for $D_1(4)$ being corrected from $D_2(4) - \nu$. In other words it represents the satellite lines if they actually do exist. In the latter case the strong lines would show denominators about 609, and 1100 above those in the table for $D_{11}(3)$ and $D_{11}(4)$. The first is about 2δ and the second of the order of 4δ , whilst if normal, judging from other cases, they should be equal. Moreover, in all other cases (In and Tl excepted) the satellite separations are practically the same multiples of the oun in the same group. Cs shows a difference of 14δ , so that the supposed ones here are far too small, as well as irregular. The observed separations, moreover, are equal within errors of observation, which would rather point to an alteration in $D_1(\infty)$. Now a lateral displacement of 2δ on $D(\infty)$ would produce a separation of $2\cdot 41$, which is about the observed value.

The table shows a stationary point at $m = 8$ and 9 and then the large fall shown in the other elements. They could be accounted for by a lateral displacement

$(2\delta_1)D(\infty)$, the mantissa of $m = 8$ being at the same time subject to the fall of multiples of δ which would scarcely stop at 14δ . In the table, however, the errors are inserted on the supposition that the mantissæ remain constant.

Cs.

The mantissæ appear to run down by equal intervals from $m = 4$ to 6, are equal for 6, 7, 8, then a large drop of about 11δ to the same value for 9, 10, and return to the value at $m = 8$ for $m = 11$. The possible errors are so large that the regularity is curious. It is possible that they might run down at equal intervals of $3\delta_1$ to the last one for $m = 10$. Or, if there are very small observational errors, the drop for 9, 10 may be due to a lateral displacement, about $(+7\delta_1)D(\infty)$. It should be noticed that with Cs all the order differences but one are multiples of $3\delta_1$, or the group multiple.

Cu.

The two first doublets of CuD are strong. The third is much weaker than would be expected. Moreover, it gives a separation between D_{11} and D_{21} of $252\cdot14$, whereas it should be somewhat less than $\nu = 248\cdot28$. This ($\lambda = 3688\cdot6$) can therefore scarcely be the normal chief line of this doublet. Now EDER and VALENTA give a spark line at $3687\cdot75$ which gives a separation with D_{21} of $245\cdot91$, leaving a satellite separation of $2\cdot37$, which is within limits in fair order with the corresponding separations in the two previous doublets, viz., $6\cdot60$ and $3\cdot39$. Moreover, the satellite separation of $2\cdot37$ gives a satellite difference of 1317 and $9\delta = 1315$, so that the normal satellite differences would run $22\delta_1$, $27\delta_1$, $36\delta_1$. This, then, would seem to be the wanting normal chief line, and it is then interesting to note that the line usually accepted as $D_{11}(4)$ is a collateral of this. The denominator difference of the two is 2474 and $17\delta = 2484$ ($\delta = 146$). Hence the K.R. line 3688 is the collateral $D_{11}(4)(-17\delta)$, and apparently the small intensity is due to the usual decrease produced by a negative lateral displacement. The modified table is taken on $\xi = -\cdot08$. It is remarkable how close the observed differences come to multiples, but little reliance must be placed on deductions from them both on account of the large possible errors and the smallness of δ_1 .

Ag.

Unfortunately the D series in Silver is poorly developed—only the first satellite has been observed, and the three chief lines after the first have very large possible observation errors. Nothing, therefore, can be learnt as to the march of the satellite differences beyond the fact that the observed— 2436 —is very close to $23\delta_1 = 2421$. In the modified table $\xi = \cdot1$, the differences are very close as is seen to multiples of δ_1 , but there can be no certainty with such large possible errors.

Mg.

In the D series of Magnesium, as arranged by KAYSER and RUNGE and as generally accepted, there are clearly certain abnormalities. $D_1(4)$ is more intense than we should expect, and its separation from $D_2(4)$ is 45.39 in place of 40.92, whilst that of $D_2(4)$ and $D_3(4)$ is very close to the exact value. This cannot be due to observational error, for this is very small (.03). Either, therefore, the true line is hidden by this bright one, which can scarcely be the case, or it is a collateral. In the former case the true line ought to be that found by deducting ν_1 and $\nu_1 + \nu_2$ from the satellites. In the second case it would require the addition of $19\delta_1$ to the denominator of $D(\infty)$, and the addition would explain the increased intensity. The two results agree, the wave numbers resulting being respectively 35054.80 and .71. The former would give a denominator .832041 in place of that in the table, but its observational error would be that of D_2 , viz., 945, while that of the collateral depends on the observed D_1 , and is 190. $D(5)$ gives normal separations within limits. $D(6)$ gives $\nu = 46.87$ and 22.15, but normal within the observation errors (2.8) [see Note 1 at end].

But there is another question which arises in connection with Mg. In the Ca sub-group the first lines have a denominator about 1.9, *i.e.*, with $m = 1$. In the Zn sub-group the lowest value of m is 2. In the MgD series, as generally accepted, the first line is $\lambda = 3838$, which requires $m = 2$. If there is a line corresponding to $m = 1$ it should be in the neighbourhood of 14900. Now PASCHEEN has observed a strong line at $\lambda = 14877.1$, but there is no triplet, which would be decisive against the allocation if we could be certain all the lines must exist. But there are cases where normal lines are observed weaker than we should expect, or are not seen at all. The well-known case of KD(3) is one example, and it is curious that if 14877 be taken as MgD(1) the denominator comes out as given in the table in a very natural order with the other denominators. The question is considered later under the F series, and the evidence there adduced is rather against the present suggestion (p. 398).

Ca.

The value of δ is calculated from Δ_2 as 58.14, $\Delta_1 + \Delta_2$ would give 58.18, practically the same. To bring the differences of the first three denominators to multiples of δ it is necessary to diminish the limit given from the consideration of the S series by 1.6 (variation limits given in [II.] = 5.8). The values can then be arranged as in the table. One result of this is to increase the value of Δ_1 (for the given $\nu_1 = 105.89$) to 2793 from 2791, which gives $\delta = 361.30w^2$ in place of 361.17, and thus closer to the adopted value 361.80. A noticeable peculiarity in this series is the very rapid falling down of the denominators after $m = 4$. It is so large and at the same time so irregular that they cannot be brought into line with the others without diminishing the limit by a large amount and by different amounts. It clearly points to the existence

of collaterals, formed by the addition of ouns to the limit $D(\infty)$. As such increase tends to increase intensity it may account for these surviving when the typical ones are either too faint or are destroyed to form the collaterals. It is useless to attempt to determine these multiples, because the observation errors are so large themselves as to be a large multiple of the oun, and at the same time we have no knowledge of what the typical $VD(m)$ should be. In general in the 2nd group the successive denominators are formed by the successive addition of smaller and smaller multiples of the oun until probably a constant value is reached. In the present case, with the quantity 155δ , that limit is certainly not reached. But it may be instructive, in order to illustrate the nature of the suggestion, to find what the collaterals ought to be if the denominators of $VD(m)$ remain the same for $m > 4$, viz., '091707. The multiples are found to be 7δ , 15δ , 33δ . The series of the observed D_{11} lines may then be exhibited by the following scheme, where d stands for '091707:—

$$\begin{aligned} D(\infty) - VD(2 + d - 99\Delta_2 - 155\delta), \\ D(\infty) - VD(3 + d - 155\delta), \\ D(\infty) - VD(4 + d), \\ D(\infty)(+7\delta) - VD(5 + d), \\ D(\infty)(+15\delta) - VD(6 + d), \\ D(\infty)(+33\delta) - VD(7 + d). \end{aligned}$$

The line $D_{12}(2)$ is interesting. PASCHEN gave it as 19859.9 with the remark "Wahrscheinlich doppelt 19856.9, 19864.6," and he allotted 19864.6 to D_{12} and 19856.9 to the Principal series. But in [II., p. 56] reasons were given against the latter allocation. In fact the line is very close (probably within observation errors) to the collateral formed by adding one oun to D_{12} . The wave-length of such would be $19857.8 = D_{12}(2)(+\delta)$ [see Note 2 at end].

Sr.

The value of δ is calculated as 277.89 from $\Delta_1 + \Delta_2 = 125 \times \delta_2$, which gives $\delta = 361.64w^2$. The differences as shown in the table are extremely close to multiples of δ . Moreover, the limits of variation for the first two are so small that the variations of ROWLAND'S standards from the correct values for his scale may become of importance. For $D(3)$ the values should be 2 less, whilst for $D(2)$, failing direct observations for reduction to *vacuo*, recourse must be had to extrapolation on KAYSER and RUNGE'S formula,* which has been done. In order to bring the differences for $D_{11}(3)$ and $D_{11}(4)$ and of $D_{11}(4)$ and $D_{12}(4)$ to multiples of δ within error limits, it is necessary to take ξ about $-.4$ or $D(\infty) = 31027.25$. When this is done the denominators can be arranged as in the table. The difference of the two

* RANDALL appears to have done this for D_{11} but not for D_{12} , which also makes his value of $\nu_1 = 392.6$ instead of 394.42 , which is close to the true value.

first denominators = 181557 = 653×278.03 . It is possible the real errors attached to $D(2)$ by RANDALL may be greater and the difference slightly less; but if we suppose 278.03 to be the real value of δ it makes $\delta = 361.82w^2$, and, therefore, very close to the adopted value. It would appear that $D_{12}(4)$ has been displaced from its normal value, judging from the irregularity introduced into the separations. If so the separations might be 14δ in place of 15δ .

Ba.

Starting with the uncertain value of $S(\infty) = 28642.63$, as given in [II.], the value of δ as calculated from $\Delta_1 + \Delta_2$ is 682.70, and from Δ_2 is 684.34, both being near the most probable values but on opposite sides. The value 683 is taken at first as a rough approximation. Apparently, the first set of lines have not been observed. RANDALL* has observed two lines, 29223.4, 23254.8, which give a separation 878.27, which is ν_1 , but no signs of satellites—or, rather, if there are satellites, the separation observed should be much smaller. If, however, the satellites have gone here, and this pair denote the first two lines of the first triplet, they depend on VD_{13} , and the value of the denominator is 2.085331,† which would range well with those of Ca and Sr, viz., 1.946, 1.987, but the second lines of these give 3.082, 3.169, and of Ba 3.093, which would rather point to a less value than 2.085 for the first line. But if $VD(2)$ is larger than $D(\infty)$, the lines would be -23254.8 for the first and -29223.4 for the second, giving a denominator for the first of 1.825551. The differences of the denominators of the D_{13} lines for $m = 2, 3, 4$, will then be 267632, 38612 instead of 6528, 38612, and are therefore more in agreement with the type of the other elements of this group. Moreover, the former, as we shall see, is a multiple of δ , whilst the other (6528) is as far out as it can be. Both values, however, are inserted in the tables (see also p. 389).

The satellite differences for $D(3)$ are 9492 ± 32 and 7516 ± 40 . The values of 14δ and 11δ are respectively 9562 ± 5 and 7513 ± 4 , and hence the first cannot be 14δ within limits of error, although it is so close as to produce a conviction that it really is so. Now for small variations of the limit $D(\infty)$ the separation differences are scarcely affected, but, as we saw in [II.], there was evidence to show that the limit $S(\infty)$ was considerably less than that found, and, in that case, the separation differences would be slightly changed. A decrease of $D(\infty)$ would increase those differences. If, however, it is so large as to bring up the first to 14δ , the second is increased so much that it is not 11δ within limits. Consequently, the two conditions confine the choice of $D(\infty)$ within very narrow limits. It is found to be close to a decrease of 32, i.e., $D(\infty) = 28610.63$. This again changes the values of Δ_1, Δ_2 , with the given values of ν_1 and ν_2 to 29379 and 11997, giving from $\Delta_1, \delta = 683.2$. The table is

* 'Ann. der Phys.,' 33 (1910), p. 745.

† The values in this and in the table are calculated from the limit as modified below.

drawn up on this basis. With these data, the suggested allocations for $D_1(2)$ give the following differences between their denominators and that of $D_{13}(3)$, viz. :—

$$\begin{aligned} \text{With } D_{13}(2) &= 29223 & 6528 &= 9.5 \times 683 \\ D_{13}(2) &= -23254 & 267632 &= 392 \times 683. \end{aligned}$$

The first, therefore, cannot be a multiple within error limits.

The values shown for $D(4)$ agree very well, but the regularity is upset. Also the actual lines have changed in appearance, and their intensities are not normal. The intensities for $D_1(3)$ are 10, 6, 4, those for $D_1(4)$ 4, 4, 6. We should expect $D_{11}(4)$ to be stronger, and certainly $D_{13}(4)$ to be much weaker. It would seem that collaterals must displace the normal lines. We have, in the foregoing pages, been led to expect that an addition of an δ increases the intensity and a deduction diminishes it. If so, we should expect a deduction in D_{11} and an addition in D_{13} . To bring $D_{11} 14\delta$ above D_{12} requires the deduction to be made in VD . This would make the typical value of the denominator greater by 2733, viz., 4.161071. In the case of D_{13} , to bring it closer to D_{12} , *i.e.*, distant 11δ , the addition would have to be to $D(\infty)$, and if so, the value of 29δ , given in the modified table, would have been a mere coincidence. But no such addition of a multiple of δ (nor of δ_1) will do this. If, however, 2δ be added to the denominator in $D(\infty)$, it is brought to separation of $10\delta + 36$, giving an error in λ for $D_{13}(4)$ of $-.02$ in place of $-.06$. If, then, δ be also deducted from VD , the separations will be 11δ . The separations would then take the form

$$\begin{array}{ccc} 423\delta & & \\ & 14\delta & 11\delta \\ 66\delta & & \\ & 14\delta & 11\delta. \end{array}$$

This arrangement is to be preferred in that (1) it explains the abnormal intensities of $D(4)$, (2) brings the separations into line with other elements. The arrangement suggested may be stated thus: if $D_{11}(4)$ and $D_{13}(4)$ represent the typical lines, the observed D_{11} is $D_{11}(4) (-2\delta)$ with decreased intensity, and D_{13} is $(+2\delta) D_{13}(4) (-\delta)$, the increased intensity due to the $+2\delta$ in $D(\infty)$ being greater than the decrease due to $-\delta$ in VD .

The results for orders >4 are similar to those of the other elements of their groups, probably collaterals of additions to $D(\infty)$.

Zn.

On account of the small values of δ_1 , and the considerable observation errors, the satellite separations in Zinc do not give decisive results. If we take the observed values for the D_{12} and D_{13} sets, the denominator differences are 489, 419 for $m = 2$, and 584, 399 for $m = 3$. Now the second sets, the D_2 , have much smaller observation

errors than the satellites of the first—see remark in the table. If the latter be calculated from them, using the accurate value of $\nu_1 = 388.90$, the differences come out to be 525, 369 and 456, 399, quite reversing the order of magnitude for the first satellite of the lines for $m = 2, 3$, and, moreover, their differences are larger than δ_1 . The differences best consonant with the measures—using the derived values from D_2 —are $13\delta_1 = 503$ and $10\delta_1 = 388$, giving a ratio of 1.30. Those entered in the table, however, are $15\delta_1 = 581$, $9\delta_1 = 348$, both within the limits of observation, and adopted because they give a ratio 5:3, the same as the other elements of Group 2. The satellite separations for $m = 3$ may be the same as the latter within limits, but not necessarily so.

The order differences do not work in well with the above when $\xi = 0$. If, however, ξ be put $= -2.25$, they fall into line with extreme accuracy, as shown in the table. It is of interest to notice that the differences are multiples of $\delta_6 = 6\delta_1$, which seems to be specially associated with zinc.

The denominators for $m = 6, 7$ are now 6.915855 (4068) and 7.924179 (11320), showing too large a rise to be due to error observations. Treated as collaterals with $-2\delta_1$ and $-3\delta_1$ they become 6.909593, 7.910070, clearly near the probable limit.

Judging from analogy, we should not expect the differences to stop at $4\delta_6$. The series $(7, 6, 4)\delta_6$ would probably be continued, but the errors are too large to settle the question. If the series were continued, *e.g.*, by $2\delta_6, 0$, the denominators would be 6.910288-695 and 7.910288-218. But the best agreement is to take them as they are. This would also be in analogy with Ca, in which $D(\infty)$ begins to change when VD stops changing.

Cd.

In the table ξ is taken .25 above $S(\infty)$, as given in [II.]. It is seen that the arrangement fits in with great accuracy, and as δ_1 is as large as 114, the arrangement may be considered to have some weight. The denominators calculated from the D_2 and D_3 lines (more accurately determined) do not agree with the observed D_1 satellites. It would therefore appear that the second and third members of the triplets may also be subject to special displacements. Here, for instance, the lines of order 3 are brought into line if the observed $VD_{21}(3)$ is $VD_{12}(3)(-\delta_1)$. The value of $D_{13}(4)$, calculated from K.R.'s $D_{31}(4)$, cannot be the normal one, even when his extreme possible error is allowed. This shows again that $VD_{31}(4)$ must be displaced from $VD_{13}(4)$, in this case by $10\delta_1$.

The denominator for $m = 6$ shows the sudden large rise after a slow change which Zn also exhibits, but it cannot be explained, as in that case, by treating it as a collateral due to a modification of $D(\infty)$ alone. The closest collateral of this type would be due to δ_1 and this changes $D(\infty)$ by 5.66 producing in the denominator a change too far in the opposite direction. In fact it becomes 6.912000, 3471 below

that of $m = 5$ in place of 5060 above. But the observation error in this line is so large that as it stands it may correspond really to a denominator equal to that of $m = 5$. If further the series of differences $75\delta_1, 31\delta_1, 12\delta_1$, be continued diminishing further as looks probable, it would come more nearly in line. For instance, as each term is about $\cdot 4$ the previous, suppose the next is $5\delta_1 = 569$. The value of $D_1(6)$ as thus calculated differs from the observed by $-.19$ while the possible error is $\cdot 30$. This would make the constancy of the denominator begin at an order one higher than in Zn. The case of Hg will be seen to support this tendency.

There are two sets of doublets, 3649.74, 3500.09, and 3005.53, 2903.24 with separations 1171.13 and 1171.95 which are clearly associated with the D series. If we write down the observed satellite separations in the $D_1(2)$ and the $D_1(3)$ lines and of D_{13} with the above we get the following scheme: 18.23, 11.10, 267.13 and 7.98, 6.18, 262.40. At first sight it makes the new lines appear as collaterals by the change of about $\frac{1}{2}\Delta_2$ on $D(\infty)$, but this cannot be the case, because a change of this amount would very considerably diminish the doublet separations below 1171. If the $D_{12}-D_{13}$ separation be deducted from that of the lines in question there results $267.13-11.10 = 256.03$ and $262.40-6.18 = 256.22$. Now the separations 11.10, 6.18 depend, as is seen above, on $11\delta_1, 15\delta_1$, so that the new lines may be written $*D(\infty)-VD_{13}(2)(-11\delta_1)-A$, $D(\infty)-VD_{13}(3)(-15\delta_1)-A$, where A is a constant which on more accurate calculation is found to be $255.80 \pm .2$. In other words, the VD of the new lines is derived from VD_{13} in the same way as that is from VD_{12} . This formula is of a type of which there has been no example hitherto. If it remained there the evidence, in spite of the curious connection with the other satellites, would scarcely be weighty enough to cause the introduction of a new departure. I hope however to show in a future communication that this expresses a very common relation between sets of lines, the constant A being in reality a composite one. The question naturally arises do the new terms give rise to an F series in the same way as the ordinary D? It should be at a distance about 267.13 in wave number above that of F. The line 15713.3 ($n = 6362.25$) is 266.90 above that of the line 16401.5 ($n = 6095.35$) which is allotted by PASCHEN to $F_3(3)$ and is clearly the first of the lines in question. There is an F(4) line at 11630.8 ($n = 8595.57$) and another at 11268.4 ($n = 8872.01$) is 266.44 above this. This may be the corresponding line sought for, but if so the line 11630 must be $F_3(4)$ and the lines $F_1(4), F_2(4)$ would then be absent. These lines were at first† assigned by PASCHEN to a new doublet set of series, but later‡ to combinations of his new singlet series with $D_1(\infty), D_2(\infty)$. This question will be considered as a whole later, but the suggested explanation given above points rather to the fact that we have to do with a triplet series in which the third number is too faint to be observed.

* $D(\infty)$ stands as usual for $D_1(\infty)$ or $D_2(\infty)$.

† 'Ann. d. Phys.,' 29, p. 650 (1909).

‡ 'Ann. d. Phys.,' 30, p. 749 (1909).

Hg.

The D series of Mercury shows a marked divergence from those of the other elements so far considered in that (1) the separations of the satellites increase as they go from the chief line, (2) the satellites do not seem to correspond in the different orders, and (3) there are a larger number. The increased tendency which this element has shown to break up into collaterals appears also here. One is led to infer that with varying conditions of the production of the light different collaterals appear.

The dependence on the δ is, however, here clearly shown, and the evidence is all the stronger because the magnitude of δ_1 itself is large (363) and because all the apparently unconnected differences come within close multiples of δ_1 . This is clearly seen in the following table where the denominator differences are exhibited together:—

$$\begin{array}{lll} 3980 = 11\delta_1 - 11 & 6909 = 19\delta_1 - 15 & 346 = \delta_1 - 17 \\ 6201 = 17\delta_1 + 32 & 6530 = 18\delta_1 + 2 & 5398 = 15\delta_1 - 45 \\ 5782 = 16\delta_1 - 20 & 6262 = 17\delta_1 + 93 & 9750 = 27\delta_1 - 48 \\ 7989 = 22\delta_1 + 6 & & 18516 = 51\delta_1 - 10. \end{array}$$

It is still possible within errors that the differences for the first satellites shall be the same as for the second and succeeding, viz., $17\delta_1$, but it is very unlikely. For the second satellites this cannot hold. It is clear that the regular law is not contradicted, but is upset by the formation of new configurations or aggregations in the oscillators.

The table is drawn on $\xi = \cdot 8$. This brings in the best agreement and, moreover, brings $S(\infty)$ —supposing it and $D(\infty)$ are the same—closer to the value found from the first three lines. The value given in [II.] being one modified slightly to bring all calculated (even for $m = 1$) within limits. The agreement is seen to be remarkably close. It is to be expected that the differences for the satellites of the same lines will be more accurate than the differences between the chief lines themselves, and this is exemplified in the table. The observation errors after $m = 6$ are too considerable to draw certain conclusions from. Apparently the denominators increase by small multiples of δ to about $m = 8$ and then remain constant.

Al.

In Al, the satellite differences deviate from the ordinary rule in that they increase with increasing order for $m = 2, 3, 4$. They are 94, 800 and 1380, and by no stretching to the extreme possible errors can the two last be made equal. The inequality is certain. Moreover, the observed differences are very close to multiples of δ . If the first satellite position be calculated from D_{21} , its difference is 110, the observed is 94 and $4\delta = 106$, 94 can be 106 within limits. D_{21} gives in the same way 800 for $m = 3$, the same as observed and 1468 for $m = 4$ instead of 1380. The last may be the same as the observed within limits, but as $52\delta = 1381\cdot 6$ and $55\delta = 1462$,

it is possible there may be this difference and $VD_{21}(4)$ is not $VD_{12}(4)$ as in the typical cases. The real difference may be any multiple between 52δ and 55δ . In fact δ is so small that there is not absolute certainty.

AID has proved itself the most intractable series to bring into any simple formula of the ordinary kind. It was, in fact, the difficulty with this element which first led me to seek another solution—on the lines now being considered.

It will be seen that it lends strong support to the theory suggested. The table is arranged with $\xi = 2.66$. The exactness of the relations there shown is very remarkable, and when it is remembered that Δ is a large number like 1754, the practically exact multiples referring to the first five lines must carry very great weight in the argument that AID at least is subject to a modification of successive denominators by multiples of certain units. The objections to the arrangement are two: (1) that $\xi = 2.66$ is outside the error limits of $S(\infty)$, and (2) the denominators appear to go on diminishing without reaching a limit. A slight alteration, however, in Δ will get over the first. For instance, if $\Delta = 1754 - .5$, ξ would be about .5 less, $D(\infty)$ would be within limits of $S(\infty)$, and the same arrangement would also hold, but it could not be much more diminished because with $m = 5$ and 6 the changes introduced into the denominators by ξ would upset the multiples 54 and 29. A change of Δ by $-.5$ would change the ratio to w^2 from 361.88 to 361.78. $D(\infty)$ is, therefore, probably very close to 48163.62.

If $\xi = -10$, the denominators tend to a limit about .107 for $m = 7$ and beyond. But this is far outside permissible limits of $D(\infty)$, and, moreover, the striking arrangement with multiples of Δ is quite upset. We must therefore conclude either that the limit is not reached until an order $m = 10$, or beyond, or collaterals enter. If the former, multiples of Δ can enter, but the observation errors are too large to give certainty. If collaterals based on $(9\delta)D(\infty)$ are used with $\xi = 2.16$ or $D(\infty) = 48163.62$ the mantissæ for 7, 8, 9 come respectively to .113569, .113590, .113956, and for 10 for a $VD_{11} = VD_{21}$, 113700. The separation observed for $m = 10$ is 107.96 instead of 112.15, either an observation error or a displacement of D_{11} or D_{21} . A displacement of D_{11} by $+2\delta$ on $D(\infty)$ brings the separation very nearly correct, although the observation error in the wave number of these two lines is as large as 4.4, it is probable their difference is much more exact and that the defect shown by $\nu = 107$ is real. (For $m = 10$, D_{11} is practically $= D_{12}$.) The results therefore go to show that the D_1 and D_2 lines for $m = 7, 8, 9, 10$ are collaterals, $(9\delta)D(\infty)$, except that for $D(10)$ an extra displacement of 2δ is added. Although the numbers above are so nearly equal we must not place too much reliance on them, as the observation errors have a very large effect on the denominators for such high orders. If the suggested arrangement is correct it must mean that K. and R.'s measurements must have been of a very high order of exactness, which would further mean that the measures for the D_2 lines would not be so exact since the observed values of the ν for $m = 7, 8, 9$ are respectively $-.68$ (possibly real on D_2), .7, .13 in error.

I am inclined therefore to think that the exact equality for $(+9\delta)$ is a coincidence, especially as the difference for $m = 6$ and 7 is not a multiple of Δ like the others. Taking the corrected $D(\infty) = 48163\cdot62$, the mantissa for $m = 6$ is $\cdot116154$, giving with $\cdot113569$ a difference $2585 = (1 + \frac{1}{2})\Delta - 46$, which is as far as it can be from a multiple of Δ .

If $+7\delta$ be taken for the collateral, and 5Δ for the difference, the limiting denominator is $\cdot107384$ and the corresponding O-C are $-.03, +.03, .07$. Now these make, as against the observed D_2 lines, the values of ν_1 about correct, which gives a certain amount of weight to this arrangement of collaterals based on $(+7\delta)$.

In the foregoing the conclusions up to $m = 6$ may be taken as well based. No definite answer can be given to the question of what happens beyond $m = 6$, although the balance of evidence perhaps points to the last, viz., collaterals based on $(+7\delta)$, and this is strengthened by considerations which follow.

MANNING* has recently observed under diminished pressure certain groups of lines which by their look suggest doublets and satellites related to the D type. The strongest set, apparently a D_{11} and D_2 doublet, are $4260\cdot05, 4241\cdot25$, giving a separation of $104\cdot05$ ($\cdot5$). If $4260\cdot05$ be treated as having the same limiting term as the D series, the denominator of the VD part comes out to be $2\cdot107364$ (21). Now this mantissa has the limiting value according to the supposition of the preceding paragraph, viz., 107384 . If this is not a mere coincidence, the connection should throw a great deal of light on the relations of these series, and would warrant a more searching discussion.

This would, however, lead too far from the immediate point at issue. It will be sufficient merely to indicate somewhat more clearly the connection. With the limit $(7\delta) D(\infty)$ the mantissa of $D_1(7)$ is 299Δ below that of $m = 2$ (see Table II.), and it should therefore be (with $D(\infty) = 48163\cdot62$) $631328(25) - 83\xi - 299\Delta$, whilst that of MANNING'S 4260 is $107364(21) - 42\xi$. If these are the same $299\Delta = 523964(46) - 41\xi$.

$$\Delta = 1752\cdot388 - \cdot14\xi \pm \cdot15,$$

and this gives $\delta = 361\cdot55w^2$, which is too small. But in this $D(7)$ of the accepted series is referred to $(7\delta) D(\infty)$, whereas 4260 is referred to $D(\infty)$. If it be referred also to $(7\delta) D(\infty)$, its mantissa is $107868(21) - 42\xi$

$$\text{and } 299\Delta = 524468(45) - 41\xi,$$

$$\Delta = 1754\cdot073 \pm \cdot15 - \cdot14\xi,$$

and therefore of the right order with $\delta = 361\cdot89w^2$.

MANNING'S new lines suggest, on a superficial glance, a series of bands, but there can be little doubt of their connection with the Diffuse series. Their relations to one another can be discussed either on the basis of the old $D(\infty)$ or of $(7\delta) D(\infty)$. With

* Observed in my laboratory, since published in 'Astrophys. Journ.,' May, 1913.

4260·05 as D_{11} (intensity 10) goes 4241·25 as D_{21} (intensity 9). $D_{21} - 112·15$ should give $D_{12} = 4261·53$. This has not been observed, but it is $D_{11}(1)(-13\delta)$. In fact, the error between this calculated value and that deduced from D_{21} is only $d\lambda = \cdot 02$, and a satellite difference of 13δ is more in accordance with that of other elements than the small one of $14\delta_1$ in the accepted series. Amongst the other lines are the collaterals $4280·4$ (intensity 9) = $(\Delta)(4260)$ with $O - C = -\cdot 04$, and $4363·7$ (intensity 2) = $(5\Delta)(4260)$ with $O - C = \cdot 1$.

In.

As in the case of Al, so In shows an increase of satellite differences with the order. The first three, 5δ , 26δ , 26δ may be considered as certain, but the next, 32δ , although it is close to the observation, may, as in the case of aluminium, be the same as the others (26δ) within error limits, owing to the large error in D_{12} . K.R. gives the difference in wave-lengths as $1·04 \text{ \AA.U.}$, whilst HARTLEY and ADENEY in the spark give it as $\cdot 4$, *i.e.*, closer. In the table it is entered as 32δ as being closer to the observations, but if it really is 26δ , the $O - C$ is $+\cdot 20$ against $O = \cdot 50$. It is possible that many cases of diffuseness may be due to the simultaneous existence of several collaterals based on differences of δ_1 , which for lines where m is large or for small wave-lengths give differences in λ too small to resolve. In this case, for instance, with $m = 5$ a displacement by δ_1 produces collaterals differing by about $\cdot 006 \text{ \AA.U.}$, and several would give the impression of a nebulous line, broadened on one side or the other. For $m = 6$ there is clearly some collateral change different in D_{11} and D_{21} . For if D_{12} be calculated from D_{21} it gives a position for D_{12} of longer wave-length than D_{11} , or the inverse of the typical order. No conclusions therefore can be drawn as to the satellite differences for $m = 6$, except that D_{21} is probably of the form $(x\delta)D_{21}$. Beyond this it is curious that the D_2 lines persist while the D_1 lines do not, which may be accounted for by their being also like $m = 6$ *additive* collaterals.

Again, also, the order differences show themselves as close multiples of δ . The table is based on $\xi = 0$, but it may be brought into still closer agreement by taking ξ a small negative number, about $-\cdot 2$ to $-\cdot 4$. The difference between 5 and 6 becoming suddenly so large (59463 order 124δ) and the entrance of the peculiarity mentioned above, suggest that some collateral influence comes in. Further, if we regard the denominators of D_2 , or of D_{12} calculated from $D_{21-\nu}$, after a small difference of 8824 , the differences begin again to increase. This has always in the previous cases pointed to a collateral displacement in $D(\infty)$. The first object is to see by what displacement the denominators may be brought to a limiting uniform value. If ξ be put -13 , the denominators for $m > 5$ become $715818, 714394, 716198, 715743, 7222, 7319$. Omitting the values for $m = 10$ and 11 , in which the probable errors are very large, it is clear that, allowing for quite reasonable observation errors, the denominators are in the neighbourhood of a limiting value. Now, a collateral of $(+2\delta_1)$ in $D(\infty)$ produces a displacement of $-13·48$, and this makes the denominator

for $m = 6$ to be $\cdot 716474$, and this is 23931 below the observed denominator for $D_2(5)$. Now, $50\delta = 23850$, which is the same as the difference for $m = 4$ and 5 instead of being less, as analogy with others would lead us to expect. But the observation errors are large (maximum of order 18δ , about) so that room is allowed for this. There would then be one step from $m = 5$ to 6 of something less than 50δ combined with a collateral displacement of $(+2\delta_1)$ on $D(\infty)$. To indicate the explanation this is entered in the table, a difference of 50δ making the denominator for $D(6) = 6\cdot 716653$. The observed abnormality as between $D_{11}(6)$ and $D_{21-\nu} \equiv D_{12}(6)$ is that the wave number of D_{11} is 1.26 less than D_{12} , whereas it should be 8 or 9 greater, with a denominator about 32δ greater instead of 1721 less. There is, in fact, a further defect beyond the normal value of about 36δ . Thus, if the difference for $D_2(5, 6)$ is $x\delta$, that of $D_1(5, 6)$ is $(x+36)\delta$. The lines would then be represented as follows:—

$$\begin{aligned} d_1 &= \cdot 755767, & d_2 &= \cdot 740503, \\ D_{11}(6) &= (2\delta_1) D(\infty) - N/\{6 + d_1 - (x+36)\delta\}^2, \\ D_2(m) &= (2\delta_1) D(\infty) - N/\{m + d_2 - x\delta\}^2. \end{aligned}$$

The collateral addition intensifies D_2 and explains its continuance, but in D_1 the increase, owing to addition of $2\delta_1$ to $D(\infty)$, is overweighted by the diminution of the excess 36δ in the VD part, and so, after the first, the rest are too faint to observe. At least, that is a suggestion of a possible explanation.

TL

In Thallium the satellite separations appear to be the following multiples of δ_1 : 24, 27, 28, 28, 28. But so far as limits of error permit, they might be 24, 27, 27, 27, 27. A peculiarity appears in the D lines in that the doublet separation for the first set is 7793.08 (48), whereas the normal value is very close to 7792.39. The difference is therefore real and not attributable to observation errors. Moreover, the next four show a gradual diminution, although still remaining normal within extreme permissible errors. The doublet values beyond this depend for the measurements of the second line on measurements of CORNU. They give separations 15 to 20 less than normal, but little reliance can be placed on deductions from them, for CORNU's results may err possibly by several units in the first decimal place, and with these small wave-lengths any error in λ is multiplied by 22 to 23 in the wave numbers. I have, therefore, not brought them into the discussion.

The table is based on $\xi = \cdot 3$, though no attempt has been made to find the best value. The mantissa of the first line is abnormal, since it is less than the second instead of greater, and, moreover, its difference from it cannot be a multiple even of δ_1 . Since the satellite difference is very close to such a multiple ($9048 = 6\delta + 4$) it is probable that the abnormality affects both in the same manner. Now the arrangement may be made normal by regarding the first line as a collateral $(\delta_1) D_1(2)$. The

addition of δ_1 to the denominator of $D(\infty)$ produces a change -19.19 , and this changes the denominator of VD to those given in the table, and as is seen now, produces a difference of $2\delta_1$ between it and the next. Now, this alteration in $D(\infty)$ diminishes the value of ν by 5.65 , whilst, as we have seen above, it is apparently $.69$ too much—or $VD_2(2)$ is $5.65 + .69 = 6.34$ below the value of $VD_{12}(2)$. Now, this is just the change made by deducting $2\delta_1$ from the denominator of VD_{12} . The exact value is 6.74 , which is within the limits. The way in which, with the considerable numbers involved ($\delta_1 = 377$), all the different abnormalities are simultaneously made to fit in with a normal scheme gives some confidence that this is the real explanation. The scheme of actual lines may be represented thus:—

$$\begin{aligned} \text{Actual } D_{11}(2) &= (+\delta_1) D_{11}(2), \\ ,, \quad D_{12}(2) &= (+\delta_1) D_{11}(-24\delta_1), \\ ,, \quad D_{21}(2) &= (+\delta_1) D_{21}(-2\delta_1). \end{aligned}$$

Contrary to the case in other elements the successive differences are equal after the first, and the limiting value of the denominator is reached at $m = 7$. They can all from 7 to 14 be, within limits, equal; but there is an apparent rise with the high orders.

O.

Two series—one of doublets and one of triplets—have been recognised in oxygen. The table shows that the D lines of both sets fall into line quite naturally with multiples of Δ_1 closely except in the case in the doublet sets of $m = 7, 8$. In both these cases the denominators are equal within limits, but much larger than those for $m = 6$ instead of being less, and the deviation is real since the difference is more than 15 times the probable error for $m = 7$, and 1.5 times that for $m = 6$, which latter has a very considerable probable error $.5$ as against $.07$.* The divergence for $m = 8$ can be accounted for, as it is probable that there are two close lines here due to different series, viz., that for this series $m = 8$ and the other for a parallel series for which $m = 5$, and may therefore be stronger. As it throws some light on the subject it may be well to say a few words about it here. RUNGE and PASCHEN give three lines at $6264.78, 6261.68, 6256.81$, with separations $7.83, 12.43$, and intensities $1, 3, 1$, so that the centre is the strongest. There is a corresponding set at $5410.97, 5408.80, 5405.08$, with the same separations within error limits and intensities $3, 4, 3$, again with the centre strongest. The strongest lines of these two triplets form a series with the observed value of $D''(8)$. They are of a diffuse type and in fact

* These are not to be confounded with K.R.'s possible errors. The possible errors are probably larger.

come between the D''' and D'' series. The limit taken is 22926·11 and the scheme is as follows:—

| | O - C. | O. |
|-------------------------|--------|-----|
| 3·969545 - 8 | ·01 | ·03 |
| $6\Delta_1$ | | |
| 4·968512 + 7 | 0 | ·04 |
| $6\Delta_1$ | | |
| 5·967480 + 24 | 0 | ·5 |

Moreover, the difference between the first denominator and the corresponding one for D''' is 2924, and this is $17\Delta_1$. It is of course understood that the digits ·11 in the limit have been chosen so that the $17\Delta_1$, $6\Delta_1$, come very close. The argument depends on the possibility of doing this. In fact RYDBERG'S tables give the limit 22926, so that the modification by ·11 is extremely slight. Thus the observed line is the line corresponding to $m = 5$ of this series, and it probably hides the weaker line of $D''(8)$. This accounts for the deviation noted above between calculated and observed in $D''(8)$. I have no explanation to offer for the corresponding deviation for $m = 7$. All the others come so close that it is difficult to imagine that this does not fall in with the rule. It is equivalent to an error in λ of about 1·2 A.U. The doublet separation for D'' is ·62 very closely, and the corresponding doublet difference is $15\delta_1 = \Delta$ say. A lateral displacement of 7Δ on the limit would just make the change, but that explanation seems out of place here. The separations 7·83, 12·43 of the new lines require denominator differences in the limit of 373 and 473, and $4\Delta_2 = 380$ and $5\Delta_2 = 475$. There is another line at 6267·06, showing a separation of 5·81 (·3). If this has the same VD as 6261 it requires a denominator difference in the limit of 277 and $3\Delta_2 = 285$. The four lines are therefore $(-5\Delta_2)(6261)$, $(-3\Delta_2)(6261)$, 6261, and $(+5\Delta_2)(6261)$.

S.

If RUNGE and PASCHEN'S estimates of their errors are valid the value of the limit of the S series is determinable very accurately. It is 20085·46 (1·34), but to bring $m = 7$ as calculated within limits it is necessary to take $S(\infty)$ more than 1 less. Accordingly the D lines have been calculated on the supposition that $D(\infty) = 20084·5$, and it cannot be far from this. To bring the differences within multiples it has been necessary to diminish this limit by putting $\xi = -·3$. The multiples then come in partly as multiples of Δ_2 and partly of Δ_1 . The value of Δ_2 given in the first part of the paper is 651, but this gives $\Delta_2 = 35 \times 180·67w^2$, whereas it should be, if the rule there established is correct, in the neighbourhood of 180·9, or $\frac{1}{900}$ larger, say 651·7. This value has been adopted in the table, although the old one can be made to fit in though not so well. The agreement is good, especially when it is remembered that K. and P.'s estimates are less than possible errors.

Se.

The lines allotted by RUNGE and PASCHEN to the D series present a quite different appearance from the normal, although there can be little doubt but that they form the SeD. The weak satellite lines after the first appear on the violet side of the strong lines, whereas in all other yet known cases they lie on the red side. Moreover, the strong lines instead of standing by themselves are each the first members of complete triplets for $m = 4, 5, 6, 7$ ($m = 4$ is the first set observed). The numbers in the table are calculated with $D(\infty) = 19274$. The value of $S(\infty)$ calculated from (4, 5, 6) is $19275.10(2.4)$, but it requires, as in S, a further diminution of over 1 (*i.e.*, within error limits) to bring in the fifth line. Hence $D(\infty)$ cannot be far from 19274. The value of δ is calculated from $\Delta_1 + \Delta_2 = 161 \times 90.40w^2$, and consequently must be considered very exact. Δ_1 and Δ_2 are calculated by transferring $15w^2$ from calculated Δ_2 to Δ_1 , making the values $28\frac{1}{4} \times 361.62w^2$ and $12 \times 361.61w^2$. The numbers calculated from the observed values are given in a separate list. A glance shows that the usual regularity is here quite upset, and one feels convinced that some disturbing influence must have been at work. If we examine the wave numbers of the first four sets as exhibited in the following table, we notice that for the first

| | | | |
|---------|--------------------------------|------------------------------|------------------------------|
| $m = 4$ | { (14149.27)? (5) 14156.19 | (3) 14252.84 (3) 14259.76 | (3) 14300.31 |
| $m = 5$ | { (6) 15803.95 (1) 15804.95 | (3) 15907.80 (1) 15908.67 | (4) 15953.89 |
| $m = 6$ | { (5) 16768.10 (1) 16769.17 | (1) 16872.15 (1) 16872.67 | (3) 16917.33 |
| $m = 7$ | { (7) 17375.92 (2) 17379.58 | (1) 17482.33 (7) 17483.00 | (3) 17523.15 (4) 17527.20 |

set, we should expect a weak satellite about 6.92 behind 14156, which is not likely to have been observed in that region far in the red. Its difference, 3129, is close to $55\delta_1 = 3118$, and provisionally we may regard this as normal. The next two triplets ($m = 5, 6$) give separations respectively 1.00 and 1.07, corresponding to a lateral displacement in $D(\infty)$ of δ_1 (δ_1 actually gives .925 displacement). For $m = 7$ the separation is 3.66 corresponding to a displacement of δ ($4\delta_1$ gives 3.7). Moreover, for this line the intensity has increased from 5 to 7 and gives suspicion of a displacement by addition. If we suppose that the chief lines have a lateral displacement $(+\delta)D(\infty)$ it means adding 3.70 to their wave numbers, *i.e.*, they are now 15807.65 and 16771.80, and they come 2.7, 2.63 in front of their satellites, which, allowing for errors in observation, is in fair order with the first separation 6.95. For $m = 7$, not only is the strong line abnormally more intense than for $m = 6$, but the faint line is so

also—which suggests they are both displaced—a suspicion increased by the abnormal increase of the difference shown in the table of denominators between 6 and 7. Provisionally the least change is to suppose the faint line displaced by δ and the strong line by 2δ , as it must, as was noted above, be δ more than the faint line.

For $m = 8$ it is curious that only one line occurs and no triplets. This suggests that there is no intensification by lateral displacement, and that provisionally it should be taken as normal. The table of difference shows an abnormal increase instead of a decrease, but this may be due to observation errors. If we now calculate the denominators for $m = 4, 5, 6, 7$, on the above suppositions, displacing the lines for $m = 9, 10$ also by δ , we get

| | | |
|----------------|-------------|---------------|
| 4·629262 (54) | 3129 | ·626133 (108) |
| 4326 | | |
| 5·624936 (56) | 2139 | ·622797 (?) |
| 4406 | | |
| 6·620530 (105) | 3475 | ·617055 (?) |
| 4216 | | |
| 7·616314 (240) | 3805 | ·612509 (480) |
| 5256 | | |
| 8·611058 (728) | | |
| 3629 | | |
| 9·607429 (643) | | |
| 9090 | | |
| 10·59833 | | |

Thus the changes indicated by the appearance and arrangement of the lines have brought the denominators and satellites into greater accord with the general rule. The practical constancy of denominator differences is exhibited also in Tl. The only outstanding irregularity appears to be the satellite difference for $m = 5$. A lateral displacement of $-\delta_1$ in $D(\infty)$ would decrease the denominator by 743, and increase the difference from 2139 to 2882. It is better to leave the difference without an attempt of explanation at present.

The second list has been drawn up on this basis, taking $\xi = -\cdot 1$ as the errors are somewhat smaller with this value. The denominator for $m = 10$ is left without further change. Another displacement of $2\delta_1$ would bring it also 19δ below that for $m = 9$, but the observation errors render any deductions quite unreliable. The

suggested scheme of actual lines may therefore be represented as follows where D_{11} , D_{12} stand for the normal type, and $D_{12}(m) = D_{11}(m) (-55\delta_1)$:—

$$\begin{array}{ll} D_{11}(4), & D_{12}(4) \\ (+\delta) D_{11}(5), & D_{12}(5) \\ (+\delta) D_{11}(6), & D_{12}(6) \\ (+2\delta) D_{11}(7), & (+\delta) D_{12}(7) \\ D_{11}(8) & \\ (+\delta) D_{11}(9) & \\ (+\delta \text{ or } +5\delta_1) D_{11}(10). & \end{array}$$

The order (4) of the first line is so large that the error limits are too wide for absolute certainty. In fact better agreement on the whole for the satellites would be obtained by taking the difference as $56\delta_1$, *i.e.*, $4\delta_{14}$, δ_{14} being specially associated with this group (see p. 331). The line 6269.28 is separated from 6266.36 by 6.44, and is therefore possibly the lateral $(+2\delta) D_{11}(5)$.

The table shows of course the known essential difference between the behaviour of the elements of Group 2 and that of Groups 1, 3, 6, signified by the signs of α in the formula. It consists in the fact that in Group 2 the orders are formed in succession by the addition of multiples, whilst in the others it is by subtraction, with the exception that Cu and Ag of Group 1 are additive. But there are certain other features which appear between the different sub-groups when higher orders are looked at. The alkalis all show a gradually decreasing decrement with a sudden dive. Na then shows a sudden rise continued for several lines, and Cs has a similar indication. Cu and Ag with only a few lines observed show decreasing increments. The alkaline earths show decreasing increments and a sudden dive (Mg excepted). The Zn sub-group shows decreasing increments and then a sudden ascent. The Al Sub-group 3 show decreasing decrements (Sc decreasing increments). O with S and Se show decreasing increments. In fact, were it not for the very clear behaviour of Zn, Cd, and Hg, the evidence would rather point to the conclusion that in each group, the low melting-point sub-group show subtraction (α positive) and the high melting-point addition (α negative). If this series depends on a formula sequence, it is difficult to see how it can be any simple algebraic one—the mantissa would rather seem to depend on a term similar to $\sin m\alpha$ or $\tan m\alpha$. In the detailed discussion above, however, it is seen how these changes of direction can be explained by lateral displacements. It is noticeable that where the irregularity observed in the first lines as compared with the others in the satellite differences appears, a similar irregularity exists also in connection with the first order differences. This is evident especially in the alkalis, where the first differences are so close to exact multiples of Δ or δ as to cause the conviction that they really are so.

It is a remarkable fact also, and one which will probably be of importance in throwing light on molecular constitution, that all those elements which do not exhibit satellites have order differences depending on multiples of Δ , whereas all the others (Al excepted) depend on multiples of the oun, δ or δ_1 . The elements without satellites are Na, K, Mg, possibly Al, both series of O, and S. All these depend on multiples of Δ_2 or Δ_1 . None of the others do so, and it may be regarded as an argument in favour of Rb possessing satellite series that its differences do not depend on Δ directly. It would appear that Rb only begins to show them for $m = 3$. For $m = 2$ the line is not split up into a chief line and satellite, the doublet separation is normal, and it is instructive to observe that the order separation between the first set and second line is close to 5Δ , and only deviates from it in the same way that is mentioned in the previous paragraph. Also Ba seems to have in the same way no satellite for $m = 2$, the separation is quite normal, and this also shows a first order difference very close to Δ_1 .* But Ca, on the contrary, which has a first difference $= 99\Delta_2$, possesses satellites.

It is noticeable also that the high atomic weight elements appear to follow more regular and simple rules. Thus both Cs and Tl show descent by equal steps in both cases $= 3\delta_1$.

The result of the discussion would seem to be that there can be no doubt but that satellite differences as well as the doublet and triplet differences depend on multiples of the oun. For the other supposition, viz., that in the Diffuse series the order differences also depend on differences of the oun, it can only be said that a case has been made out. The supposition in all cases fits conditions, but the conditions are not all sufficiently definite to give certainty. After the first two or three orders the observation errors are larger than the δ_1 , and even for these the value of δ_1 for the low atomic weights is comparable with the errors. In some of these cases, however, multiples of Δ which is much larger enter and strengthen the argument. The strongest examples are those of the alkaline earths (small errors and large Δ or δ_1), first lines of Cd, and Hg, Al (series in Δ), In, Tl, and the Δ series of O and S.

The D(2) Term.—If the foregoing theory of the constitution of the Diffuse series is correct, it is further necessary, in order to complete the discussion, to determine the origin of the first term. The apparently close relation of the F series to the D series, and the several cases of collaterals of the former which had been noted with large multiples of Δ , suggested a trial to see if the denominators were multiples of this quantity. As in cases where satellites are present, the separations depend on them and not on the strong line, it is natural to expect that the satellite is a normal line and the strong line a collateral, and this is found to be justified by the calculations on this theory. In Table III. the first column of figures gives the value of the denominator taken from Table II. The second column gives the factors together with possible variations. Thus the denominator of $KD_{11}(2) = .853302$. This has

* But see discussion of BaF below.

TABLE III.

| | | | |
|----|---|---------------------|---------|
| Na | $D_{11} \cdot 988656$ | | |
| K | $D_{11} \cdot 853302 = 291 (2932 \cdot 27 \pm \cdot 130 - \cdot 364\xi) = 291\Delta$ | 361·944 | 362·68 |
| Rb | ? $D_{12} \cdot 766216 (?) - 8\delta = 59 (12950 \cdot 84 \pm 2 \cdot 74 - 1 \cdot 44\xi) = 59\Delta$ $- 10\delta = 59 (12942 \cdot 06)$ | 361·991 361·746 | 361·40 |
| Cs | $D_{12} \cdot 546989 = 857 (638 \cdot 260 \pm \cdot 233 - \cdot 0887\xi) = 857\delta$ $D_{11} \cdot 554286 = 17 (32605 \cdot 06 \pm 13 \cdot 41 - 4 \cdot 47\xi) = 17\Delta - 10\delta$ | 361·785 | 361·74 |
| Cu | } Theory of constitution uncertain. | | |
| Ag | | | |
| Mg | $D_1 \cdot 828688$ | | 362·36 |
| Ca | $D_{13} \cdot 945972 = 691 (1368 \cdot 99 \pm \cdot 03 - \cdot 047\xi) = 691\Delta_2$ | 361·84 | 361·84 |
| Sr | $D_{13} \cdot 987349$, not a multiple. $D_{12} \cdot 989572 = 178 (5559 \cdot 39 \pm \cdot 25 - \cdot 20\xi) = 178\Delta_2$ | 361·738 | 360·02 |
| Ba | $D_{13} \cdot 825511 = 69 (11963 \cdot 9 \pm ?) = 69\Delta_2$ * $D_{13} 1 \cdot 041954 = 87 (11976 \cdot 4) = 87\Delta_2$ | 361·968 362·352 | 362·34 |
| Ra | Not observed. = $31\Delta_2$.† | | |
| Zn | $D_{13} \cdot 904978 = 260 (3480 \cdot 68 \pm \cdot 38 - \cdot 430\xi) = 260\Delta_2$ | 361·682 | 362·25 |
| Cd | $D_{11} \cdot 902039 = 87 (10368 \cdot 26 \pm \cdot 26 - 1 \cdot 276\xi) = 87\Delta_2$ D_{13} , not a multiple. | 361·382 | 361·392 |
| Eu | $D_{13} \cdot 917794 = 50 (18355 \cdot 88 \pm ? - 2 \cdot 28\xi) = 50\Delta_2$ | 361·44 | 360·93 |
| Hg | $D_{13} \cdot 921662 = 31 (29731 \cdot 0 \pm 1 \cdot 22 - 3 \cdot 80\xi) = 31\Delta_2$ | 361·50 | 362·46 |
| Al | $D_{11} \cdot 631287 = 360 (1753 \cdot 575 \pm \cdot 069 - \cdot 230\xi) = 360\Delta$ $D_{12} \cdot 631181 = 360 (1753 \cdot 280 \pm \cdot 069 - \cdot 230\xi) = 360\Delta$ | 361·777 361·717 | 361·879 |
| In | $D_{12} + 16\delta = 22 (37676 \pm 2 \cdot 18 \pm 4 \cdot 619\xi) = 22\Delta$ | 361·871 | 361·947 |
| Tl | $D_{12} = \cdot 888344 = 590 (1505 \cdot 667 \pm \cdot 136 - 1 \cdot 881\xi) = 590\delta$ $D_{11} \text{ coll.} = \cdot 899520 = 597 (1506 \cdot 73 + \cdot 136 - 1 \cdot 881\xi) = 597\delta$ | 361·650 361·913 | 362·063 |
| O | $D''' \cdot 972483 (40) - 120\xi$ 46 (171·66 ± ?) = 46Δ_1 $D'' \cdot 980380 (92) - 121\xi$ 63 (172·063) = 63Δ_1 New D ·969543 | 362·46 ± 363·308 | 361·79 |
| S | $D_1 (4) \cdot 553446 = 530 (1044 \cdot 24 \pm \cdot 088 - \cdot 811\xi) = 530\Delta_1$ | 362·113 | 362·14 |
| Se | $D_1 (4) \text{ observed} \cdot 629262 = 99 (6356 \cdot 18 \pm \cdot 54 - 4 \cdot 565\xi) = 99\Delta_1$ | 361·893 | 364·00 |

* See below under discussion of BaF—two different triplets in question.

† See below under discussion of RaF.

observation errors and also possible error due to incorrectness of $D(\infty)$, *i.e.*, ξ . These give the denominator as $291(2932.27 \pm .130 - .364\xi)$. Now 2932.27 is very close to 2939, which is given as the approximate value of Δ in Table I. The denominator is then written 291Δ , and with this new value of Δ the corresponding value of the oun is calculated as $361.944w^2$ instead of the old value $362.68w^2$, which for comparison is entered next to it.

Notes on the Tables.

Na. Δ is so small that several multiples of it might be taken for D within limits.

Rb. D_1 does not give a multiple of Δ although close to it. If, however, Rb has satellites, the denominator for D_{12} will be a few multiples of δ less than that of D_{11} . That for Cs is $11\frac{1}{2}\delta$ less in the corresponding case. The values in the table are given for 8δ and 10δ . Judging from the value of the oun it is probably near 8δ . In any case the multiple would be 59Δ . This is a very strong argument that Rb does possess satellites.

Cs. Neither D_{11} or D_{12} give multiples of Δ .

Mg. As in Na, Δ_2 is too small, and the denominator too large to give anything definite.

Sr. D_{13} gives the oun clearly too small, although better than in the original table. D_{12} , however, gives a value 361.738 quite close to the probable value. A similar result is shown also by Cd which occupies an analogous position in the next sub-group. If D_{13} behaves in what appears to be the normal manner, it would appear necessary to take the atomic weight to be .10 less than BRAUNER'S value, *viz.*, 87.56 in place of 87.66, which is probably too large a change to be acceptable.

Ba. In Barium the first set is doubtful. That taken above shows no satellites. The denominator is therefore that for D_{13} , and this is a multiple which gives a value of the oun much nearer the probable value than that in Table I. Evidence will be given later however under BaF that there is a normal satellite triplet, outside the region of observation, where D_{13} has the denominator 2.041954, which, from analogy with the other elements of this group, has a "mantissa" 1.041954, and this is again a multiple of Δ_2 . This, therefore, is probably the correct value, and the other set will be collaterally displaced from this by $18\Delta_2$.

Ra. The first line should be far in the ultra red, and has not been observed. The multiple $31\Delta_2$ is determined indirectly (see BaF below).

Cd. This element shows the same irregularity as in Sr, in that D_{13} does not give an exact multiple of Δ_2 , although one close to it. Here, however, we have to go back to D_{11} before finding the exact multiple, and D_{11} gives almost the precise value of the oun as in Table I., which was itself very exact.

Eu. D_{13} is .917794, which is $50\Delta_2 + 1344$, Δ_2 having the value 18329 of Table I. If it is $50\Delta_2$ exactly, Δ_2 would be $18355.88 - 2.28\xi$, making the oun ($361.46 - .04\xi$) in place of 360.93 of Table I., a great improvement.

Hg. D_{13} gives denominator = 31×29731.0 , and the latter factor is

$$7410.87w^2 = 82 \times 90.375w^2,$$

which is much closer to the probable value of the oun, and moreover 82 is the correct multiple to give $54 \times 543.816w^2$ for $\Delta_1 + \Delta_2$, which has been taken as a basis for δ . This value of Δ is supported by the discussion of the F series below.

Al. As the order differences are all multiples of Δ , and there may therefore be some doubt as to the real existence of satellites the values for D_{11} and D_{12} are inserted. The denominators for the two only differ by $4\delta = 108$, or the observed by 96. As the Δ differences can only refer to the D_{11} set, it would seem that these should be taken as the normal lines giving 361.777 as the value of the oun.

In. Neither D_{11} nor D_{12} are exact multiples of Δ although they are very close to 22Δ . D_{12} is 1722×477.11 , or 1723×476.83 . If these be taken as multiples of the oun, they give the oun as 362.01 and 361.80 in place of 361.94 of Table I., but the multiples are too large to found any conclusions upon. It would rather seem that there is some displacement from a typical multiple. Using Δ as given in Table I., viz., 37684, $22\Delta = 829048$. So that $D_{12} = 22\Delta - 7455$ and $7455 = 16\delta - 177$. If it is $22\Delta - 16\delta$ exactly, Δ becomes 8.04 less and the oun 361.871 w^2 in place of 361.947. The value of $D_{12} + 16\delta$ is therefore inserted. If the typical term were 16δ higher, the order differences would run $72\delta, 62\delta, 50\delta, 50\delta$, in place of $58\delta, 62\delta$, &c., and hence more in line with others.

Tl. Neither the observed nor the supposed collaterals are multiples of Δ . They are expressed as multiples of δ . Although they are large multiples, their values are quite definite provided we know *a priori* that the denominators are multiples as a fact. If the multiple be altered by unity, the resultant quotient cannot come within the limiting values of the oun.

If the normal $D_{12}(2) = 7\Delta = 939078$, the order difference over $D_{12}(3)$ would be $939078 - 888643(89) = 50435 \pm 89$, and $33\frac{1}{2}\delta = 134\delta_1 = 50495$, so that the order difference would come out as usual a close multiple of δ_1 . All this group seem to show the same kind of irregularity.

O. There are three separate series, see data for Table II., differing by multiples of Δ_1 , just as in the order differences. Δ_1 is too small to test the multiples of the denominators themselves.

S. The D(2), D(3) lines for S and Se are beyond observed regions. Sulphur however shows no satellites, and we may surmise therefore in analogy with others that the differences for D(2), D(3), D(4) are like the others multiples of Δ_1 or Δ_2 . As a fact, $D_1(4)$ is a clear multiple of Δ_1 , and the surmise is justified so far as Δ_1 is concerned. The value of ξ is not very certain.

Se. Se apparently has satellites, and the order differences are only multiples of δ . It should not therefore be expected that $D_1(4)$ or $D_2(4)$ should be a multiple of Δ_1 . Nevertheless $D_1(4)$ is clearly such a multiple and is entered in the table.

The table shows that where triplets occur the multiples are those of Δ_2 and not of Δ_1 , except in the case of the oxygen group of elements, in which Δ_1 clearly takes the place of Δ_2 . If the law of multiples is correct, the values of the Δ obtained in this way must clearly be far more exact than those obtained direct from the separations. A glance at the deduced values of the δ compared with the former values shows how much closer to the mean value 361.9 the new ones are than the old, and to some extent this adds to the weight of the evidence. The cases where the multiples do not appear to enter are those of Rb, Cs, In and Tl. The case of Rb has been considered above and a natural explanation offered. Cs, In and Tl have all large values of δ , in which case we have already seen a tendency for the spectra to depend on smaller multiples of the δ than the Δ . In the case of Cs, the δ is smaller than the multiple and it can give no evidence nor data for the δ . The case is different however for Tl. If the δ enters, the multiple can be no other than that given, and as is seen the value of the δ is improved. All the elements of the Al group show a deviation from the normal type in that the first satellite separations are much smaller for the first order lines than for the second, and seem to point to some displacement. As the Al orders differ by multiples of Δ , any irregularity in the multiple between the first and second orders does not alter the dependence of the denominator on the multiple of Δ . In In and Tl, however, the differences go by multiples of δ or δ_1 , and any irregularity on them will throw out the dependence of the first denominator on a multiple of Δ . As was shown above the addition of 16δ in In not only produces the multiple, but at the same time shows a more usual march of differences for the orders. In Tl the observed denominator for $D_{12}(2)$ is less than that for $D_{12}(3)$ and quite abnormal. The other anomalies occur in that in Sr, D_{12} appears to take the place of D_{13} , and in Cd, D_{11} . RaD (2) is in the ultra red and has not been observed. The elements Na and Mg must be left out of account because the ratio δ/Δ must be so large that a number of multiples can be found all giving Δ within observation limits. Cu shows a multiple, but the theory of the constitution of the series of Cu and Ag is doubtful and must also be left out.

With the above doubtful cases the values for K, Ca, Sr, Ba, Zn, Cd, Eu, Hg, Al, S and Se, are clearly exact multiples, and the large values of Δ in Ba, Cd, Eu and Hg show that these multiples are real. This rule, exhibited as it is in so many cases, and in by far the majority of the elements comparable, must correspond to a real relation and cannot be due to mere coincidence. Against the reality of the relation is the antecedent improbability that those elements with the smallest value of Δ should have the largest values of the denominator, as *e.g.*, in the case of Na and Mg. A possible explanation is that the mantissa is the nearest multiple of Δ_2 to some group constant. But see also under discussion of the F series. It might however have been expected on this ground that the denominators would be of the form $1 - M(\Delta)$. But the case of Na is clearly against this. Its denominator $.988656 = 1 - .011344$ and 11344 is 15.26Δ and cannot be a multiple. It would seem conclusive that the

denominators of the extreme satellites of the first line are multiples of Δ_1 or Δ_2 and that explanations should be sought for apparent exceptions.

The S and P Series.

The relationships between the doublet and triplet sets of the P series and between the S and P series were discussed in [II., p. 51] by comparing the differences between the corresponding denominators. It is now possible to see how, if at all, these differences are related to the *oun*.

The P Series.—In the alkalis the differences between the corresponding denominators of the two sets were found to be constant within error limits and of course equal to Δ . In the other elements in which the P series have been allocated, there was always a drop in the difference, which in several cases then remained constant for the succeeding orders. The values were given on [II., pp. 51–53]. They are reproduced here, and it is seen at once how they proceed on quite analogous lines with successive satellite differences of the D series considered above. The possible errors of the single lines from which they are deduced are given in brackets. Thus ZnP (1) are 1·599352 (2), 1·592143 (3), 1·588669 (4), and the differences are given as 7209 (2, 3), 3474 (3, 4). The higher orders, in which the possible errors are so large as to be themselves multiples of δ_1 , are not included. The value of δ_1 is given with the symbol for the element.

It will be noticed that the more accurate the observations the closer are the differences to the multiples of the *oun*. But the observed variations from true multiples in the case of the large separations would seem to point to a difference in the α as well as in the μ . In any case it would seem that μ must alter *per saltum* from order to order, unless the sequence formula is a complicated function of m .

| Zn ($\delta_1 = 38\cdot75$). | | Cd ($\delta_1 = 113\cdot8$). | | | |
|--------------------------------|-----------------|--------------------------------|-------------------|----------------|---------------|
| 7209 (2, 3) | 3474 (3, 4) | 23109 (4, 5) | 10368 (5, 5) | | |
| 12 δ –5 | 6 δ +20 | 50 δ_1 –5 | 30 δ_1 –26 | | |
| 5355 (19, 28) | 2525 (28, 36) | 17423 (25, 25) | 6980 (25, 25) | | |
| δ +9 | 3 δ_1 –5 | } 3 δ_1 +27 | } 5 δ_1 +4 | | |
| 5191 (9, 9) | 2414 (9, 9) | | | 18269 (922) | 6461 (1837) |
| δ_1 –1 | δ_1 | | | 17109 (26, 28) | 6407 (28, 25) |
| 5154 (30, 30) | 2375 (30, 30) | | | | |

Hg ($\delta_1 = 362\cdot87$).

| | |
|-------------------|--|
| 87815 (?) | 30002 (?) |
| 11 δ –118 | 14 δ_1 +143 |
| 71967 (?) | 24779 (?) |
| 2 δ_1 –122 | 3 δ_1 –126 or 2 δ_1 +237 |
| 71364 (?) | 23817 (?) |

Note how Zn still affects δ_6 . The variations from multiples in Hg seem to have relation to the transference properly noted above, viz., from Δ_1 to Δ_2 .

| Al ($\delta_1 = 26\cdot57$). | Tl ($\delta_1 = 376\cdot835$). |
|----------------------------------|------------------------------------|
| 1751 (?) | 134154 (?) |
| 16δ_1-3 | 53δ_2+191 |
| 1329 (78, 78) | 94018 (?) |
| -2δ_1+5 | 2δ-191 |
| 1377 (23, 23) | 91195 (?) |
| 0-3 | 2δ_1-173 |
| 1380 (48, 48) | 90615 (?) |

In Al the value after the first is 1381 within limits of error for all.

The S and P Connections.—The differences of the corresponding denominators in the S and P are also given in [II.]. The values are, however, subject to uncertainties due to uncertain limits in both S and P, in which the ξ are not the same for both. In the case of the alkalis there seems a very clear connection with the Δ , except in Cs, where as often before δ enters. In the other elements it was shown that the sequences are inverted and the differences are to be taken between the first of the S and the second of the P. In Al, Tl, and Zn, there is again a clear relation, but it is now to the denominator differences of the $P_1(2)$ and $P_2(2)$, or 1329, 94018, 2525 respectively, say Δ' for each. In the case of Cd and Hg no clear relation is apparent, although they behave approximately like Al and Tl. This want of exact agreement may be due to the effect of the transference inequalities considered above (p. 333) in connection with the δ . The relations indicated above are shown in the following scheme, in which the differences for the S and P are taken from [II., p. 51-53].

| | |
|--------------|---|
| Na | $\cdot490162 = \cdot5 - 13\Delta,$ |
| K | $\cdot464597 = \cdot5 - 12\Delta,$ |
| Rb | $\cdot487501 = \cdot5 - \Delta,$ |
| Cs | $\cdot491944 = \cdot5 - 14\delta$ (roughly). |
| Al | $\cdot489330 = \cdot5 - 8 \times 1334 = \cdot5 - 8\Delta',$ |
| Tl | $\cdot594887 = \cdot5 + 94887 = \cdot5 + \Delta'.$ |
| Zn | $\cdot528306 = \cdot5 + 11 \times 2573 = \cdot5 + 11\Delta',$ |
| Cd | $\cdot526358 = \cdot5 + 26358,$ |
| Hg | $\cdot603628 = \cdot5 + 103628.$ |

The F Series.

In Part I. the symbol F was used to denote the series whose limit depends on the values of VD (2) in a similar way to that in which the limits of the S and D series depend on VP (1). Where the D series show satellites the F series in consequence consist of doublet or triplet series with constant separations. They comprise some of the strongest lines in the respective spectra, but as in general they occur in the ultra-red region they have not received the same attention as the other better known ones. In the alkaline earths, however, they come well within the visible regions, and show strong sharply defined lines. They are related also to other strong lines by collateral and other displacements depending on considerable multiples of Δ , and so naturally come under discussion in the present communication. As will be seen later, the discussion gives the means of obtaining very accurate determinations of the Δ —and consequently of the ν —as well as of settling other questions. I propose, however, not to attempt an exhaustive discussion in the present communication, partly because the main object now is only to illustrate the influence of the ν , and partly because it would seem that a large number of lines which clearly belong to the F cycle are related in a manner neither ordinal nor collateral, nor according to RITZ'S combining theory.*

For convenience of reference the wave-lengths of these lines are given in the Appendix, together with short historical notes.

The Alkalies.—The table below gives the denominators for the two first lines in each as calculated from PASCHEN'S and from RANDALL'S results. BERGMANN'S measurements for other lines are too much in error for the present objects. The limits used are the calculated values of VD, using the limits $D(\infty)$ given in Table II. above and the values of $D(2)$ in the Appendix.

| Na. | K. | Rb. | Cs. |
|-------------------------------|------------------------------|------------------------------|----------------------------|
| 3·997919 (169) – 219 ξ , | 3·992817 (252) – 290 ξ , | 3·987849 (433) – 289 ξ , | 3·977334 (146) – 287 ξ |
| 4·997267 (2845) – 569 ξ , | 4·989237 (696) – 566 ξ , | 4·983697 (846) – 564 ξ , | 4·9698 |
| | | | 5·9710 |
| | | | 6·9642 |

The question that first arises is, do these refer to actually the first lines of the series? If, like D, the lowest value of m were 2, the wave numbers of the lines would be somewhat above, Na, 0; K, 1200; Rb, 2060; Cs, 4450. For Na it would be outside, but the others come within regions observed by PASCHEN.†

He gave for K lines at wave numbers 1346·3 and 1182·9. The former requires a

* The relation is extremely common in certain types of spectra, *e.g.*, the rare gases other than He. I hope to return to this in a future communication.

† "Zur Kenntnis ultraroter Linienspektren III.," 'Ann. d. Phys.,' 33 (1910), p. 717.

denominator 3'007542 and the latter 2'987479, the one apparently too large and the other too small to fit in with the progression of the lines for $m = 3, 4$. But the mantissa for the latter is within limits 2δ below that for $m = 3$ [see Note 3 at end].

In Rb there is a line at wave number 2129'0 which would require a denominator 2'997805, well in step with the other two. PASCHEN identifies it as $D_{12}(3) - P_2(4)$, assuming the existence of satellites in RbD. It would seem to be more probably the $F(2)$ sought for. There is another line given as 2156'1 or 2164'4. If the former is the more correct it gives denominator = 3'001138. In Cs no line appears with wave number near 4450. There are two lines, however, with wave numbers 3409'93 and 3321'37 which differ by $88'56 \pm '6$, and certainly suggest the doublet series depending on the $D(2)$ satellite. This requires a separation of 97'96, and if they belong to the F series there must be a satellite with a separation $9'40 \pm '6$ which we should not expect to observe as being too faint. The lines give a mantissa 2'851708 with a satellite difference 1003. The latter may be, within limits, 2δ , a value which in the alkaline earths seems to be closely associated with F satellites. But the mantissa is less than that for $m = 3$, when a larger value should be expected. Even if not $F(2)$ itself it may be related to the F cycle in a similar way to certain displacements found in the alkaline earths (see pp. 383, 413), and it should be noted that if so there seem to be lines in corresponding positions in K and Rb. They are (in wave numbers) the 1182'9 referred to above for K and 1911'05 in Rb. The latter requires a denominator 2'971391. In this connection it is interesting to note that PASCHEN makes the remark that this line at times shows itself double. The separation calculated from his numbers is 1'12, giving a denominator difference of 107 for $F_1(\infty)$ and $F_2(\infty)$, *i.e.*, for $VD_{11}(2)$ and $VD_{12}(2)$. This would indicate a sort of incipient satellite in RbD. These considerations seem to show that there is some likelihood that $m = 3$ does not give the first line of the F series, and they will be felt to have greater weight when the curious irregularity in the $F(2)$ of the alkaline earths to be noticed immediately is taken into account. The question is further discussed on p. 397 in connection with the other elements.

The next question is, is there any indication of F satellites in the accepted lines? If so we should only expect to find it in Cs. Now RANDALL gives weak lines 8080'9 close to 8083'1, $F_1(4)$, and 8018'9 close to 8020'6, $F_2(4)$. They look like satellites only on the wrong side. The first changes the denominator by 2000, which is within easy limits of $1914 = 3\delta$. It will be shown that this is a common satellite difference in the alkaline earths. Further, it makes the denominator 4'9718, thus bringing the values for $m = 3, 4, 5, 6$ in order, which is not the case in the table above. There is, therefore, something to be said in favour of taking the normal $F(4)$ doublet to be at 8080'9, 8018'9, and that that is then collaterally displaced by 3δ to the stronger lines 8083'1, 8020'6. It is also quite in keeping with analogy in the alkaline earths that a similar displacement is not shown in the case of the first lines $F(3)$ (if $F(3)$ are the first lines).

Group II. The Alkaline Earths.—The series are most fully and regularly developed in Ca and Sr. In Ba and Ra the configurations which give rise to the normal type seem to be so modified that displaced lines become common, and in cases the normal line has disappeared. On the other hand, Mg seems to range itself with the Zn sub-group. It will be best therefore to deal with Ca and Sr first, and as they are built on a precisely similar plan to consider them together.

The following table gives the wave numbers of the series together with certain others which are clearly similarly related in the different elements. The separations are indicated by thick figures. The wave-lengths are given in Appendix II.

| Ca. | | | | | Sr. | | | | |
|----------|--------------|----------|--------------|----------|----------|---------------|----------|--------------|----------|
| 16203·40 | 21·75 | 16225·15 | | | 14801·57 | 101·73 | 14903·30 | | |
| 16204·72 | | | | | | | 15046·98 | 61·70 | 15108·68 |
| 21799·02 | 21·13 | 21820·15 | 13·58 | 21833·73 | | | 20530·76 | 59·78 | 20590·54 |
| | | | | | 20432·18 | 100·64 | 20532·82 | | |
| | | | | | 20435·10 | | | | |
| 24391·49 | 21·50 | 24412·99 | 13·66 | 24426·65 | 23045·78 | 99·26 | 23145·04 | 58·54 | 23203·58 |
| 25793·67 | 21·64 | 25815·31 | 13·55 | 25828·86 | 24457·06 | 100·05 | 24557·11 | 59·25 | 24616·36 |
| 26634·00 | 22·43 | 26656·43 | 14·29 | 26670·72 | 25303·32 | 100·47 | 25403·79 | 58·61 | 25462·40 |
| 27177·76 | 21·58 | 27199·34 | 15·09 | 27214·43 | 25850·61 | | | | |

Analogous Sets in Ca and Sr.

| | | | | | | | | | |
|----------|--------------|----------|--------------|----------|----------|---------------|----------|--------------|----------|
| 17847·46 | 21·94 | 17869·40 | 13·86 | 17883·26 | 18061·87 | 100·20 | 18162·07 | 56·61 | 18218·68 |
| 17887·55 | 21·81 | 17909·34 | | | 18239·35 | 100·62 | 18339·97 | | |
| 18968·53 | 21·58 | 18990·10 | 14·01 | 19004·11 | 19016·64 | 100·34 | 19116·98 | 59·75 | 19176·73 |

| Ba. | | | | | Ra. | | | | |
|-------------------------|---------------|-------------------------|---------------|----------|----------|---------------|----------|---------------|----------|
| 13089·79 | 260·60 | 13350·39 | | | | | | | |
| 13471·69 | 259·76 | 13731·45 | 157·55 | 13889·00 | | | | | |
| 13477·44 | | | | | | | 17793·09 | | |
| 18686·80 | 255·17 | 18941·97 | | | 17300·80 | 699·93 | 18000·73 | | |
| 21308·19 | 252·51 | 21560·70 | 148·32 | 21709·02 | | | 22037·41 | 456·64 | 22494·05 |
| | | | | | 21350·92 | 701·89 | 22052·81 | | |
| 22706·84 ⁽¹⁾ | | 22979·57 | | | | | | | |
| 23667·07 ⁽²⁾ | | 23919·27 ⁽³⁾ | | 23995·83 | | | | | |

⁽¹⁾ F₁₂(5)(Δ₂).

⁽²⁾ F₁(6)(9Δ₂).

⁽³⁾ F₂(6)(8Δ₂).

It is clear that these lines also show satellites. Also, it is curious that the first sets of triplets apparently have the lines corresponding to the second separation displaced below those forming the first. Thus in Ca the second set (giving $\nu_2 = 13.5$) have not been observed, in Sr the two ($\nu_1 = 101, \nu_2 = 60$) are separated by a gap of 143, and a similar effect will be found later in Ba. Owing to this fact, the formulæ constants are calculated from the 2nd, 3rd, and 4th sets. They give for F_{11} —

$$\begin{array}{l} \text{Ca} \quad . \quad . \quad . \quad . \quad . \quad 28934.93 - N \left/ \left(m + .891511 + \frac{.086641}{m} \right)^2, \right. \\ \text{Sr} \quad . \quad . \quad . \quad . \quad . \quad 27612.37 - N \left/ \left(m + .875560 + \frac{.100548}{m} \right)^2. \right. \end{array}$$

These give the following values of O—C:—

| m . | 2. | 6. | 7. |
|--------------|-------|-----|-----|
| Ca | -1.18 | .18 | .22 |
| Sr | - .42 | .05 | .02 |

The agreement is good, except for $m = 2$, and in this case the agreement is sufficient to show that the allocation for $m = 2$ is correct.

The limits are close to those of $VD_{11}(2)$, which is not known with great exactness because the values of $S(\infty)$ or $D(\infty)$ given in [II.] for the second group are subject to possible errors of some units. With formulæ in $1/m$ the values of $D(\infty) = S(\infty)$ are given [II., p. 36] as 33994.85 for Ca and 31037.27 for Sr, whilst with formulæ in $1/m^2$, the respective limits are 33983.45, 31027.64. The values of VD_{11} deduced from these are respectively 28939.93, 27615.65 with $1/m$ and 28928.53, 27606.02 with $1/m^2$. The limits, therefore, found above for $F_{11}(\infty)$ lie each between their corresponding values as deduced from the D series direct. Assuming that the $F(\infty)$ are more accurate, the values of $D(\infty)$ deduced from them are 33989.85 for Ca and 31033.99 for Sr, in both cases close to the mean of those in [II.]. If the series depend on formulæ sequences, these limits may be taken as close to the correct values. If, however, the different orders proceed by multiples of δ or Δ in the way illustrated in Table II. for the D series, the limits may require modification by a few units.

As the separations of the F series depend on the separations of the satellites of the first lines of the D series, and these depend on displacements by definite multiples of δ , as given in Table II., it is possible to calculate the values of the former with extreme accuracy. Table II. gives 13δ and 8δ as the multiples in question for both the elements Ca and Sr. Using the values of δ and of the denominators of D_{11} there given, the separations in question calculate out to 22.49, 13.75 for Ca and 100.34, 62.01 for Sr. These may be regarded as exact to the 2nd decimal place and independent of any possible variation of ξ .

In the case of Ca the observed lines, with differences somewhat less than 22·49 and 13·75, seem to indicate the presence of close satellites. If 16203·40 is really $F_{12}(2)$, the separation of the first satellite is 1·32, with possible errors ($\cdot 26 \pm \cdot 26$), which form a very considerable proportion of the total amount. A displacement of 3δ produces a separation of 1·51 and it may be this. But 16203·40 has an excessive intensity for a satellite line, viz., 6, as against 4 for F_{11} , and, moreover, it may possibly be the collateral $S_1(2)(-\Delta_2)$ which gives $O-C = \cdot 03$ with $O = \cdot 10$. If the latter allocation is correct, it would hide F_{12} , which should be $16225\cdot 15(\cdot 26) - 22\cdot 49 = 16202\cdot 66(\cdot 26)$, giving a separation of 2·06 ($\cdot 52$) due to 4δ which gives 2·02. The same considerations applied to the second set give a separation of 1·36 for the first satellite, in which again 4δ gives 1·26, and $\cdot 22$ for the second, δ giving $\cdot 32$. The separations are so small that no certain conclusions can be drawn as to their origin. The actually observed numbers may be due to 4δ and δ , but 3δ and 2δ are just possible [but see Note 4].

For Sr the first doublet is useless, as the line is due to the early measurements of LEHMANN, which are affected with considerable errors. The observed separation for F_{11} and F_{12} gives 101·73 instead of something less than 100·34. The second triplet gives 2·92 for the separation of the second satellite from the first and 2·06 for the separation of the satellite of the second line of the triplet, and from analogy with other satellite series, this would be the separation of the first and second satellites of the first line. Differences of 3δ and 2δ give separations of 3·06 and 2·04, so that it may be concluded that the satellites depend on these differences, a conclusion supported by the fact that a similar result is indicated as possible for Ca.

Returning to the curious fact noticed above that the first triplets of the series seem to be dislocated, the second fragment in Sr is found at a distance 143·68 below its normal position. For the present we note this can be explained by one of two possible collateral displacements, viz. $(-18\frac{1}{2}\delta) F(2)$ or $F(2)(3\Delta_2)$, where F stands for the normal F_2 or F_3 . The case of Ba below will give evidence in favour of the latter explanation.

In addition to the lines of the series itself, there are two sets of triplets and a doublet which are clearly analogous in the two elements. They are given in the list above, following the series lines. The first triplets in each are curious as having the middle line the strongest.* They are also related to others in the way indicated in the following scheme:—

| | | | | | |
|----|--------------|--------------|--------------|--------------|---------------|
| | | | (8) 17847·46 | | |
| | | | 21·94 | | |
| Ca | (8) 17842·52 | 13·98 | (8) 17856·50 | 12·90 | (10) 17869·40 |
| | | | | 13·86 | |
| | | | | | (8) 17883·26 |

* A similar peculiarity has already been noted in the associated OD series.

| | | | | | | |
|----|---------------|--------------|---------------|---------------|---------------|---------------------------|
| | | | | (6) 18061·87 | | |
| | | | | 100·20 | | |
| Sr | (6) 18044·71 | 59·69 | (8) 18104·40 | 57·67 | (10) 18162·07 | |
| | | | | | 56·61 | |
| | | | | | (8) 18218·68 | |
| | | | (10) 18968·53 | | | |
| | | | 21·57 | | | |
| Ca | (8) 18985·31 | 4·79 | (6) 18990·10 | 7·15 | (6) 18997·25 | |
| | | | 14·01 | | | |
| | | | (4) 19004·11 | | | |
| | | | (10) 19016·64 | | | |
| | | | 100·34 | | | |
| Sr | (10) 19083·27 | 33·71 | (8) 19116·98 | 15·25 | (8) 19132·23 | 10·70 (8) 19142·93 |
| | | | 59·75 | | | |
| | | | (4) 19176·73 | | | |

The first lines of the triplets give as denominators, supposing the true limits to be $F_1(\infty) + \xi$ —

| | Ca. | Sr. |
|-------------------|--|---|
| 1st triplet . . . | $3\cdot145123(22) - 141\cdot8\xi$ | $3\cdot388848(28) - 177\cdot4\xi$ |
| 2nd „ . . . | $3\cdot317300(30) - 166\cdot4\xi$ | $3\cdot572008(23) - 207\cdot8\xi$ |
| | $\frac{172177 + 30p - 22q - 24\cdot6\xi}{= 126(1366\cdot48 + \cdot24p - \cdot17q - \cdot20\xi)}$ | $\frac{183160 + 23p - 28q - 30\cdot4\xi}{= 33(5550\cdot30 + \cdot69p - \cdot85q - \cdot91\xi)}$ |
| | $= 126(1368\cdot78 - \cdot20\xi) - 5\delta$ | |

where p, q lie between ± 1 . Clearly the differences are the multiples $126\Delta_2, 33\Delta_2$, for the two elements respectively.

The first lines of the doublets give for Ca $3\cdot150824(22) - 142\cdot6\xi$ and for Sr $3\cdot420693(18) - 182\cdot5\xi$.

These differ from the denominator of $F_{11}(3)$ by

$$\begin{aligned} \text{Ca.} \quad & 769567 + 123p - 22q - 132\cdot6\xi = 562(1369\cdot33 + \cdot22p - \cdot04q - \cdot236\xi) \\ \text{Sr.} \quad & 488383 + 32p - 18q - 90\xi = 88(5549\cdot81 + \cdot36p - \cdot20q - 1\cdot02\xi). \end{aligned}$$

That is, they apparently differ by $562\Delta_2, 88\Delta_2$ respectively. We shall see shortly that the best value for ξ makes the relation for Sr very exact, whilst that for Ca is more doubtful.

The following list contains the wave numbers of certain lines related to the F series in the two elements with the denominators appended for the chief lines:—

| | Ca. | | | Sr. |
|------------|--------------|-------------------------------------|---------------|-----------------------|
| | | | -31237.30 | |
| | | | 100.84 | |
| α_1 | | | -31338.14 | 1.363986— 11.56 ξ |
| | | | -31345.01 | |
| | | | 68.93 | |
| | | | -31413.94 | |
| | | | 99.99 | |
| α_2 | | | -31513.93 | 1.361954— 11.51 ξ |
| | | | -15380.80 | |
| | | | 13.92 | |
| | | | -15394.72 | |
| | | | -15447.35 | |
| | | | 21.75 | |
| A | -15469.10 | 1.571602— 17.7 ξ | | |
| B | - 5011.98 | 2.141121 | | |
| | 5014.74 | } 22.71 2.141244— 44.7 ξ | 8894.66 | 2.420625— 64.7 ξ |
| | 5034.69 | | | |
| | 10.06 | | | |
| | 5044.75 | | | |
| C | 6171.18 | 2.194987— 48.2 ξ | | |
| | 21.12 | | | |
| | 6192.30 | | | |
| D | 13133.01 | 2.634565— 23.3 ξ | 15271.72 | 2.981157 |
| | 20.04 | | 99.09 | |
| | 13153.05 | | 15370.81 | |
| E | 15580.59 | 2.865778—107.7 ξ | | |
| | 20.66 | | | |
| | 15601.25 | | | |

| | Ca. | | Sr. | |
|---|--------------|-----------------|---------------|-----------------|
| F | 17847·46 | 3·145123—141·8ξ | 18061·89 | 3·388848—177·4ξ |
| | 21·94 | | 100·18 | |
| | 17869·40 | | 18162·07 | |
| | 13·86 | | 56·61 | |
| | 17883·26 | | 18218·68 | |
| G | 17887·55 | 3·150824—142·6ξ | 18239·35 | 3·420693—182·5ξ |
| | 21·81 | | 100·62 | |
| | 17909·34 | | 18339·97 | |
| H | 18968·53 | 3·317300—? | 19016·64 | 3·572008—207·8ξ |
| | 21·57 | | 100·34 | |
| | 18990·10 | | 19116·98 | |
| | 14·01 | | 59·75 | |
| | 19004·11 | | 19176·73 | |
| I | | | 21022·14 | 4·048761 |
| | | | 59·91 | or |
| | | | 21082·05 | 1·499227 |

From these we find the following differences, m denoting the mantissa only:—

| | Ca. | Sr. |
|---|--------------------------------------|--------------------|
| $a_2 - a_1$ | | 3δ within limits |
| m of F— m of a_2 | | 5 (5378·80—33·2ξ) |
| m of D— m of A | 46 (1368·75—1·43ξ) | |
| m of G— m of B | 7 (1368·71—14ξ) | 68—118ξ = 0 |
| m of $F_{13}(3)$ — m of F | 562 (1368·82—·236ξ) | 88 (5549·81—1·02ξ) |
| H—F | 126 (1366·48—·20ξ) | 33 (5550·30—·91ξ) |
| | 126 (1368·78—·20ξ)—5δ | |
| D—C | 321 (1369·40+·51 $d\lambda$ —·110ξ)* | |
| G— $F_{13}(2)$ † | 158 (1368·89—·173ξ) | 89 (5558·90—·77ξ) |
| G— $F_{12}(2)$ ‡ | 158 (1368·16—·173ξ) | 89 (5552·66—·77ξ) |
| E—D | 169 (1368·12—·144ξ) | |

Also the first triplet A in Ca shows the same kind of dislocation as in F(2) of the other elements. The dislocation is 52·63, corresponding to a denominator difference of 931, and 16δ is 930.

* $d\lambda$ on 13133 may be > 1.

† $F_{13}(2)$ as calculated from the formula.

‡ Allowing 2δ for the satellite difference $F_{12} - F_{13}$.

The number of the cases where multiples of Δ_2 enter, as well as their appearance in the corresponding position in the two elements where corresponding lines are observed must produce a conviction that they represent real and not chance relations. In the case of Ca it makes Δ_2 close to 1368.7 corresponding to $\delta = 361.77w^2$. If ξ has any but a very small value, the first two multiples are upset, but these may be due to chance. If ξ be made -6.5 as suggested below, Δ_2 will be about 1370.2 with $\delta = 362.15w^2$, which is considerably greater than the most probable value. The probability is that ξ can only be a small \pm quantity, $\xi = \pm 1$ changing δ/w^2 by $\pm .06$. A similar reasoning applied to Sr rather tends to show that here the value -6.5 is to be preferred. It makes the first multiple $= 5 \times 5594.60$, and the other values of Δ_2 become 5556.44, 56.21, 57.66, and 5556 gives $\delta = (361.52 \pm .24)w^2$, the uncertainty of this being due to a possible error in the atomic weight of 87.66, with $\xi = -5.5$ the first relation gives $\Delta_2 = 5561.40$.

Again the most probable values of the denominators of $F_{13}(2)$ are

$$\begin{aligned} \text{Ca} &= 934539^* - 115.2\xi = 937277 - 115.2\xi - 2\Delta_2, \\ \text{Sr} &= 925946^\dagger - 114.0\xi = 937060 - 114.0\xi - 2\Delta_2. \end{aligned}$$

The numbers on the right are practically equal. If analogous relations are found in Ba and Ra it points to the existence of a group constant about 937300. On the other hand it would seem that the denominators of $VF_{11}(2)$ are, like those of $VD_{13}(2)$ multiples of Δ_2 also, for

$$\begin{aligned} \text{denominator of CaF}_{11}(2) &= 934539 + 5\delta = 683(1368.71 - .16\xi), \\ \text{,, ,, SrF}_{11}(2) &= 925946 + 5\delta = 167(5552.79 - .68\xi), \end{aligned}$$

and $\xi = -6, 5$ in Sr makes $\Delta_2 = 5557.21$ in line with those above.

$$\begin{aligned} \text{The denominator of CaF}_{11}(2) &\text{ is } 8\Delta_2 \text{ less than that of CaD}_{13}(2), \\ \text{,, ,, SrF}_{11}(2) &\text{ ,, } 11\Delta_2 \text{ ,, ,, ,, SrD}(2). \end{aligned}$$

Which of these two interpretations is the more likely must be left until the cases of Ba and Ra are considered. It should however be noted that there may be some uncertainty as to what lines really represent F_{11} , F_{12} , or F_{13} , *i.e.*, as to which of them the multiple law is to be attached.

There remains to consider the question of the real limits. The reasons for supposing them to be D_{11} , D_{12} , D_{13} are so strong that it is necessary to see whether the values obtained direct from the F series, and those required in Table II. cannot be brought into agreement.

If the F series possess what has been called in [II.] a formula sequence, the values obtained for $F(\infty)$ above cannot be more than a few units in error, and in this case it

* Calculated from formula.

† The observed is probably $F_{13}(2)$ since the separation with $F_2(2)$ is the full value.

must be possible to raise the limits for $D(\infty)$ to agree with those calculated from $F(\infty)$. That is, to raise that for Ca from 33981.85 to 33989.85 and for Sr from 31027.25 to 31033.99, or Ca by 8.00 and Sr by 6.74 or thereabouts. It may probably be possible to find numbers near those which would still make the order differences of Ca and Sr multiples of δ , but only by supposing that the successive mantissa-differences in the D series after rising begin to decrease with higher orders, which is against the rule in other cases. This is so far an argument against this way of reconciling the different values of the limits. If however the order differences in the F series behave in a similar manner to that considered above for the D, *i.e.*, by multiples of δ or Δ , the exactness of the $F(\infty)$ found by means of a formula is no longer so close, and the question becomes one of seeing if, when they are made 8 less for Ca and 6.74 for Sr, it becomes possible to arrange the denominators in the same way.

If the attempt be made to reduce $F(\infty)$ by 8 in CaF, a similar objection to that raised above will enter, *viz.*, the successive mantissa-differences after falling begin to rise after $m = 5$. If however a reduction of about 6.5 be made, reducing the limit to that found in [II.] for $S(\infty)$, the order mantissæ differ successively within observation limits by $10\Delta_2, 4\Delta_2, \Delta_2, \Delta_2, 0$. Further, in the case of Sr a fall of 6.75 produces a similar fall and rise in successive denominators. If however ξ be put -1.33 , the mantissæ differences become within limits $3\Delta_2, \Delta_2 + 9\delta, 16\delta, 11\delta, 4\delta$. If this is justified, it is curious that as in the D series where there are no satellites, the differences proceed by multiples of Δ_2 the same rule should hold for CaF, where satellites are at least not certain. The difficulty can only be stated and the solution left open. It is possible that the order differences must be compared from the F_{12} of one line to the F_{11} of the next, for which there is evidence in Ba and Ra.

Barium.—In discussing Ba we start under the disadvantage that the lines belonging to D(2), with the corresponding satellite separations have not been observed, for the ultra-red doublet treated in the discussion on the D series does not seem to belong to the normal D(2). Moreover, the observed lines which are clearly related to the F series are so dispersed by collateral displacements that it is questionable whether it is possible to arrange a series proceeding by an algebraical sequence as in the other cases. The lines exhibited in the table above run on parallel lines with the corresponding lines in Ca and Sr, and are clearly closely related to the successive orders of the series, even if they are not the typical ones themselves. An attempt to obtain a formula from the first three gives a limit = 25906.7, and gives a value of the wave number for $m = 5$ of 22729.52 close to the strong line 22706.84. It is 250.05 behind the strong line 22979.57, which indicates that the last is probably the normal $F_{21}(5)$, and makes the normal $F_{11}(5)$ about 250 behind. This is in fair order with the march of the others. We may therefore feel justified in settling that the limit of $F_1(\infty)$ is near 25906.7. The F separations are close to 260 and 157, they are therefore based on satellite differences in the D series of 15δ and 9δ ; δ is so

large that there can be no doubt. These numbers are in analogy with the values for Ca and Sr, viz., 13δ and 8δ , are in the usual ratio $5:3$, and stand to the observed values for BaD (3) given in Table II. in a similar relation to those in Sr. Now $F_3(\infty)$ must be $VD_{13}(2)$, and if the general rule found above that the mantissa of $VD_{13}(2)$ is a multiple of Δ_2 holds, it is possible to obtain a very accurate value. As a fact, with $F_1(\infty) = 25906$ the mantissa of $F_3(\infty)$ is very nearly the multiple of $87\Delta_2$. If it is made so exactly, taking $\Delta_2 = 11960$, then $F_1(\infty)$ becomes about 25922. This value, with the D satellite differences of 15δ , 9δ , give

$$\begin{aligned} F_1(\infty) &= 25922 \\ &\quad \mathbf{260\cdot17} \\ F_2(\infty) &= 26182\cdot17 \\ &\quad \mathbf{157\cdot95} \\ F_3(\infty) &= 26340\cdot12 \end{aligned}$$

and it is seen how close the separations come to those observed. If we put $F_1(\infty) = 25922 + \xi$, the mantissa of

$$D_{13}(2) = 1\cdot040539 - 38\cdot7\xi = 87(11960\cdot2 - \cdot45\xi) = 87\Delta_2.$$

The D(2) lines calculated from these and $D_1(\infty) = 28610\cdot63$ found above give the following scheme in wave-lengths on ROWLAND'S scale *in vacuo*:—

| D ₁ . | D ₂ . | D ₃ . |
|------------------|------------------|------------------|
| 44042·97 | 31758·94 | 28416·75 |
| 41178·36 | 30241·91 | |
| 37193·67 | | |

The last one only comes within the region in which RANDALL'S ultra-red lines lie, his longest wave-length being 29223, belonging to the doublet treated as a possible D line above. If the rules employed are valid, these values can only err by a few units. The denominator of $VF_{11}(2)$ is $2\cdot923500 - 113\cdot9\xi$. In the cases of Ca and Sr there is apparent the existence of satellites, viz., $F_{12}(2) = F_{11}(2)(-3\delta)$ and $F_{13}(2) = F_{11}(2)(-5\delta)$, and in both cases the mantissa of one of the $F_1(2)$ sets thus found are multiples of Δ_2 . If this is general the mantissa for $BaF_{13}(2)$ will be $920085 - 113\cdot9\xi$. This is $77(11949\cdot1 - 1\cdot48\xi)$, sufficiently near to give some weight to the allocation. If $\xi = -10$ this is $77 \times 11963\cdot9$ and the value for D_{13} given above becomes $87 \times 11964\cdot7$, giving a value of $\Delta_2 = 11964$ within limits of error. $\Delta_2 = 11964$ makes the own $683\cdot66 = 361\cdot98w^2$ with $W = 137\cdot43$. The F satellites thus constituted would, if existing, have separations for $m = 2$ of $18\cdot02$ and $12\cdot03$, and for $m = 3$ of

7.63 and 5.09—but they have not been observed for $F(2)$ —as indeed is the case in Ca and Sr the first set in which show separations of the full amount. The curious dislocation of the second half of the triplet from the first seen in Sr shows itself here also. The analogue appears to be shown in the triplet coming next in the list which appears to have kept its first member and satellite. The displacement is $381.06 \pm$. This cannot be due to a displacement in $F(\infty)$, for if so the separations due to 15δ , 9δ , would be considerably larger. If it is treated as a displacement on VF the denominator difference is $43403 - 5.3\xi$, while $3\Delta_2 + 11\delta = 43414$. It is probably therefore this. The corresponding displacement in Sr was found to be $3\Delta_2$. The separation between the first line and the satellite is 5.75, the satellite being due to LEHMANN whose measures are not very accurate, it may well be 6.01 corresponding to a satellite difference of δ . The lines may therefore be represented

$$\begin{aligned} F_{11}(2)(3\Delta_2 + 11\delta), & \quad F_{21}(2)(3\Delta_2 + 11\delta), & \quad F_{31}(2)(3\Delta_2 + 11\delta), \\ F_{11}(2)(3\Delta_2 + 12\delta). & & \end{aligned}$$

If the next two lines are correctly allocated, 18686 should have an unobserved satellite with a difference 2δ . This would make 18941.97 or $F_{21}(260.26)$ ahead of the satellite, so that this supports the allocation. The line $21308.19 = F_{11}(4)$ corresponds to a satellite with 5δ . This makes, on the supposition of satellite differences of 2δ , 3δ , 21560.70 or $F_{22}(4)(260.89)$ ahead of the satellite $F_{13}(4)$, the satellite $F_{12}(4)$ being absent. The line for $m = 5$ appears to be displaced to 22706. The value calculated from the rough formula gives a line 250 behind the strong line 22979.57, clearly showing that the latter is a $F_2(5)$ line, and 22706 is very close to a displacement of Δ_2 on the calculated. If this be made exact the undisplaced line would be at 22719.97, or 259.60 behind 22979.57. This is within error limits of 260.17. Hence $F_{12}(5)$ has been altogether displaced to $22706.84 = F_{12}(5)(\Delta_2)$, and 22979.57 is $F_2(5)$. For $m = 6$ the formula gives $F_1(6) = 23582.83$. There is a doublet at 23667.07 (.28), 23919.27 (1.14) with a separation 252.20, and no others in the neighbourhood. If these are the displaced $F(6)$, the normal $F(6)$ would be 23595.82 and 23855.93 and the observed lines $23667.07 = F_1(6)(9\Delta_2)$ and $23919.27 = F_2(6)(8\Delta_2)$. The calculated normal lines have separation 260.11, or practically 260.17. A line at 23995.83 is 413 = 260 + 153 ahead of the calculated $F_1(6)$. It is therefore the undisplaced $F_3(6)$.

There are a large number of other lines clearly related to the F type. Their complete discussion would require a more searching investigation than can be given now. Several sets are related in a manner which is quite common in spark and rich arc spectra, indicated by the fact that a number of lines may differ in succession by nearly the same separation—a kind of relation which cannot be due to collateral displacement by equal denominator differences. There are a few also which seem to be attached parasitically to S and D lines. There may be uncertainty also as to

whether the separations shown which differ from 260 and 158, differ through a satellite effect, or by successive collaterals of 15δ and 9δ . For instance, putting

$$15\delta = \Delta', \quad F_1(\infty) - F_1(\infty)(\Delta') = 264\cdot10, \quad F_2(\infty)(-\Delta') - F_2(\infty) = 256\cdot39, \\ F_2(\infty)(-2\Delta') - F_2(\infty)(-\Delta') = 252\cdot35,$$

all which separations occur. In the lines now to be referred to, however, the separations will be supposed to owe their defect from 260 to the satellite effect, and thus treated it is clearly seen what an important rôle the Δ_2 term plays.

Amongst the ultra-red lines observed by RANDALL* appear the following in wave numbers:—

$$1. \left\{ \begin{array}{l} (70) 9387\cdot55 (4\cdot4) \\ (60) 9547\cdot08 (1\cdot82) \\ (60) 9771\cdot54 (\cdot95) \\ (5) 9804\cdot787 (1\cdot5) \\ (60) 9964\cdot527 (3) \end{array} \right\} \begin{array}{l} 159\cdot93 \\ 257\cdot70 \\ 159\cdot76 \end{array}$$

The figures in brackets before the numbers give intensities and those after the estimated maximum errors. They clearly belong to the F cycle, and show within error limits the normal separations. The run of the intensities would point to negative values, with the first four respectively for $f_{31}, f_{21}, f_{11}, f_{12}$, but also the 2nd, 4th and 5th might be f_1, f_2, f_3 , whereby 9771 would not come in and the small intensity for f_2 would be abnormal. On the first supposition, $f_{11} = -9771$ gives a denominator $1\cdot752908(23) - 24\cdot5\xi$ and $f_{12} = -9804 = f_{11}(-\delta)$. On the second, $f_{11} = 9547$ gives a denominator $2\cdot588000(143) - 79\xi$. Now

$$752908(23) - 24\cdot5\xi = 63(11950\cdot3 \pm \cdot36 - \cdot36\xi) = 63(11961\cdot1 \pm \cdot36 - \cdot36\xi) - \delta,$$

or denominator of $f_{12} = 63(11961\cdot1 \pm \cdot36 - \cdot36\xi) - 2\delta = 63\Delta_2 - 2\delta$.

In the following the wave numbers of some sets of lines with their separations are given. The low frequencies have been observed by LEHMANN and by HERMANN and HOELLER. LEHMANN gives many weaker ones not observed by HERMANN and *vice versa*. LEHMANN's observations were earlier but are not nearly so accurate as those of the others.

| | | | | | |
|----|----------|---------------|----------|---------------|----------|
| 2. | 12636·36 | 260·17 | 12896·53 | | |
| 3. | 14141·15 | 260·94 | 14402·09 | 158·63 | 14560·72 |
| 4. | 14903·26 | 254·37 | 15157·63 | 157·88 | 15315·51 |
| | 14934·33 | | | | |
| 5. | | | 16921·93 | 156·03 | 17077·96 |
| | 16669·61 | 259·69 | 16929·30 | | |

* 'Ann. d. Phys.,' 33, p. 745 (1910).

| | | | | | |
|-----|----------|---------------|----------|---------------|------------|
| 6. | 17219·30 | 262·78 | 17482·08 | | |
| 7. | 17508·93 | 261·16 | 17770·09 | | |
| 8. | 18577·96 | 258·12 | 18836·08 | 144·15 | 18980·23 ? |
| 9. | 18585·56 | 255·92 | 18841·48 | | |
| 10. | 18632·62 | 261·69 | 18894·31 | | |
| 11. | 23667·07 | 252·20 | 23919·27 | | |

The following numbers give the corresponding denominators calculated from $F_1(\infty) = 25922$. Where the separation differs from 260, the satellite value—or, which is the same thing, the denominator for F_{21} —is inserted as well, but, in order to distinguish it, it is printed further to the right—the changes due to ξ being the same for both.

| | | | | |
|--------------|-------------------------------|---|--|---------------|
| (2) | $2\cdot873178 - 108\cdot1\xi$ | } | 95506 = 8 (11938·3 - 1·39\xi) | 11952 |
| $F_{11}(2)$ | $2\cdot923500 - 113\cdot9\xi$ | | | |
| $F'_{12}(2)$ | $2\cdot967999 - 119\cdot2\xi$ | } | 83165 = 7 (11880·7 - 1·49\xi) | 11895 (11969) |
| | $\delta + 3$ | | | |
| $F'_{11}(2)$ | $2\cdot968684 - 119\cdot2\xi$ | } | 108209 = 9 (12023·2 - 1·58\xi) | 12039 (11982) |
| (3) | $3\cdot051164 - 129\cdot5\xi$ | | | |
| | $\cdot051267$ | } | 28667 = 24 (11944·6 - 1·76\xi) | 11962 |
| | $\cdot154087$ | | | |
| | $5\delta_1 - 46$ | } | 107563 = 9 (11951·7 - 1·99\xi) | 11971·6 |
| (4) | $3\cdot154916 - 143\cdot1\xi$ | | | |
| | $26\delta_1 + 18$ | } | 60060 = 5 (12012 - 2·08\xi) | 11964·6 |
| | $3\cdot159373 - 143\cdot7\xi$ | | | |
| | $\cdot441229$ | } | 60060 = 5 (11943·8 - 2·08\xi) + 2\delta_1 | 11964·6 |
| (5) | $\cdot441583$ | | | |
| | $2\delta + 5$ | } | | |
| | $3\cdot442954 - 186\cdot0\xi$ | | | |
| (6) | $3\cdot549987 - 203\cdot9\xi$ | } | | |
| | $3\delta_1 + 13$ | | | |
| | $\cdot550517$ | } | | |
| (7) | $3\cdot610577 - 214\cdot5\xi$ | | | |
| | $\delta_1 + 43$ | } | | |
| | $\cdot610791$ | | | |

| | | | | | |
|------------------------|---|-----------------------------|--|---------------|--|
| (8) | { | .863911 | | | |
| | | $2\delta_1 + 14$ | | | |
| | | $3.864437 - 263\xi$ | | | |
| (9) | { | .865855 | | 14463 | $= 11929 + 15\delta_1 - 28 - 3.1\xi$ 11932 |
| | | $3.866436 - 263\xi$ | | | |
| (10) | { | $3.878900 - 266.1\xi$ | | | |
| | | .879299 | | 14495 | $= 11933 + 15\delta_1 - 2.9\xi$ 11962 |
| $F_{12}(3)$ | | .892050 | | | |
| $F_{11}(3)$ | | $3.893395 - 269.0\xi$ | | 978143 | $= 82(11928.5 - 3.16\xi)$ 11970 |
| $F_{12}(4)$ | | .871538 | | | |
| $F_{11}(4)$ | | $4.875553 - 528.3\xi$ | | 968996 | $= 81(11962.9 \pm 5.93 - 4.63\xi)$ |
| $F_{12}(5)(-\Delta_2)$ | | $5.840534 - 908.3\xi$ | | 964981 | $= 81(11913.3 \pm -4.63\xi)$ 11959.6 |
| | | $\Delta_2 - \delta - 14$ | | 976927 | $= 82(11913.7 - 4.63\xi)$ 11960 |
| $F_{12}(5)$ | | $5.851797 - 908.3\xi$ | | | |
| ? $F_{11}(5)$ | | .852480 | | | |
| (10) | { | .961761 | | | |
| | | Δ_2 | | | |
| | | $6.974086(432) - 1546.4\xi$ | | | |

The differences are given in thick figures. The last column gives the corresponding value of Δ_2 without regard to observation errors when $\xi = -10$. In the case of (3) if the differences be referred to a hypothetical F_{11} , displaced 3δ from 14141, the two abnormal values come to 11969 and 11982. It will be remembered that we had an indication above of $\xi = -10$ with $\Delta_2 = 11964$ in treating both $VD_{13}(2)$ and $VF_{13}(2)$ as depending on multiples of Δ_2 . It would seem, therefore, that the value of Δ_2 is close to 11964 ± 3 and the value of $F_1(\infty) = 25912$.

The actual differences of successive denominators in the normal series may thus be represented:—

$$\begin{aligned}
 F_{11}(2), F_{12}(3) &= 81(11957.4 - 1.91\xi) = 81(11940.6 - 1.91\xi) + 2\delta, & 11959.7, \\
 F_{11}(3), F_{12}(4) &= 82(11928.5 - 3.16\xi) = & , 11960.1, \\
 F_{11}(4), F_{11}(5) &= 82(11913.7 \pm 3.6 - 4.63\xi) & , 11960.0 \pm 3.6,
 \end{aligned}$$

in which the last column also gives the value of Δ_2 , where $\xi = -10$.

The first multiple of 81 with addition of 2δ suggests (1) a real $F_{11}(2)$, displaced 2δ from 13089, or (2) that there is a normal type F_{11} about Δ_2 behind. The latter may well not be a typical F_{11} line since it makes the exact separation 260 with F_{21} . There

is a line by LEHMANN at 13096·55, but its collateral displacement cannot be 2δ within any likely limits of even LEHMANN'S measurements. As to the second supposition, there is a line at $n = 12992\cdot53$ by LEHMANN which gives denominator $2\cdot892050$. This gives a difference with $F_{12}(3)$ of $82(11943\cdot5 - 1\cdot90\xi)$, which with $\xi = -10$ would again make $\Delta_2 = 11962\cdot5$. It would thus appear that the normal $F_{11}(2)$ line is 12992, and the system receives a double displacement, first to 13089, and again to 13471. The mantissa is $912483 - 112\cdot6\xi$. The addition of $2\Delta_2$ makes it $936403 - 112\cdot6\xi$, which with $\xi = -10$ is 937529, well within error limits of the same quantity in the case of Ca and Sr. Again we are met with the apparent simultaneous existence of two explanations which cannot be compatible. Is the true explanation that the typical first line is $937300 - 2\Delta_2$, but that the corresponding configuration is not very stable and transforms to one depending on the nearest complete multiple of Δ_2 . Certainly such instability is indicated in Ba.

Radium.—The discussion for radium is rendered even more uncertain than that for barium, in that the ultra-red region has not been observed, the process of disintegration and re-aggregation has proceeded further, and, in addition, there is some uncertainty about $\Delta_2 = 37\delta_2$ adopted.

RUNGE and PRECHT'S plates were only sensitive up to 6500 Å.U., and EXNER and HASHEK give only two lines above this, 6642·73 and 6641·38, both of which belong to the F cycle. The number of lines, however, coming within this cycle is very large, but a complete discussion would involve the consideration of the new kinds of relationships referred to under barium, and cannot therefore be undertaken here. It will be sufficient to deal only with some generalities, specially bearing on the series proper, which will also give some further light on the general D series.

There are a large number of triplets with separations in the neighbourhood of 692 and 432, which are roughly in the proper ratio 5 : 3, allowing for the fact that the actual separations must be larger. Those in the table of F lines above are roughly parallel to the BaF, and give a limit somewhere about 24520. $VD_{11}(2)$ would therefore be about this, and $VD_{13}(2)$ more than $692 + 432 = 1124$ larger. The denominator of $VD_{13}(2)$ should be a multiple of Δ_2 . Using the most probable value of $\Delta_2 = 37\delta_2$, it is found that the denominator comes out very close to a multiple of $31\Delta_2$. If this be made exact it is found that $VD_{13}(2) = F_3(\infty) = 25752\cdot75$. The value of $F_3(\infty)$ is then taken $25752\cdot75 + \xi$. The values of δ are so large that there can be no ambiguity about the multiples to be chosen to give the separations, viz., 16δ , 10δ . These multiples march well with those for Ca, Sr, Ba. The separations resulting are 705·93, 456·69, with $F_1(\infty) = 24590\cdot13$ and $F_2(\infty) = 25296\cdot06$. If we apply the rule shown in the preceding elements for $F_{13}(2)$, the denominator is $2\cdot937300 - 2\Delta_2 = 2\cdot868676$. Satellites depending on 3δ , 2δ would give separations 51·44 and 34·20, and the fact that these separations occur in connection with $n = 17300$ renders the identification of that for F(3) rather doubtful, a doubt which is increased when we test the allocation by the law indicated above that the

differences of the denominators of $F_{11}(m) - F_{12}(m+1)$ is always the same multiple of Δ_2 , as is done below. The line 19897 has separation 689.33, and therefore should have a satellite (too faint) 16.60 above it. Allowing for observational errors on 19897 this is 5δ on the denominator. The following scheme will then illustrate the law of formation:—

| | | | |
|------------------------|-------------------|---|---|
| Calculated $F_{13}(2)$ | 2.868676 | | |
| Satellite | 3.837028 | } | — 993288 = 29(34251 ± 14 - 9.05ξ), 34296 ± 14 |
| | 3½δ | | |
| 17165.94 | 3.843521 - 258.8ξ | | |
| 17236.68 | 3.861964 - 262.6ξ | | |
| | 9δ | } | — 993464 = 29(34257.4 - 8.8ξ), 34301 |
| 17300.80 | 3.878913 - 266.1ξ | | |
| Satellite | 4.825655 | } | |
| | 4.830492 | | |
| | 2δ | } | — 993158 = 29(34246.8 - 13.2ξ), 34312 |
| 19897.05 | 4.834202 - 515ξ | | |
| 21350.92 | 5.818813 - 898.2ξ | | |

In the above the first is the denominator calculated from $937300 - 2\Delta_2$. It is affected with an uncertainty of about 400 on the 937300. The line $n = 17165.94$ has a separation 680.84 with 17846.78, and therefore should have a satellite 25.09 above it. Its denominator difference is 6493 behind and $3\frac{1}{2}\delta = 6492$. The line 17236.68 is associated with 17300. Its denominator is 16949 behind that of 17300 and $9\delta = 16695$ —the same within limits. The satellite of 19897 is displaced $4\frac{1}{2}\delta$. There is no evidence of a satellite 2δ behind it, but the difference of $29\Delta_2$ is made with this suppositious one. It is seen that a value of ξ about -5 makes these the same within limits. The corresponding values of Δ_2 are appended in the last column. It may be taken that the discussion has established that the satellite differences in the lines RaD(2) are 16δ and 10δ . This is the only result of which there can be certainty.

The Zn Sub-group.—Using the limits given in Table II. above and the corresponding values of $D_1(2)$, the limits $F_1(\infty) = D(\infty) - D_{11}(2)$ come as follows:—

| | | |
|------------|----------------------------|-------------------|
| Zn | 12988.37, with separations | 4.38, 3.74. |
| Cd | 13022.83 | „ „ 18.23, 11.10. |
| Hg | 12753.07 | „ „ 34.68, 62.04. |

PASCHEN allots the following for Zn and Cd, viz., in wave numbers:—

| | | | | |
|--------|---------|-------------|----------------------|--------------|
| | 6059·50 | | 6065·51 | |
| | | 3·05 | | 17·86 |
| ZnF(3) | 6062·55 | | CdF(3) | 6083·37 |
| | | 2·43 | | 11·98 |
| | 6064·98 | | | 6095·35 |
| | | | CdF ₃ (4) | 8595·57 |

The line 8595 must be allotted to F₃ because it makes the difference 266 with 8872, so that the two are F lines connected with D₁₃(2) and the companion to the D₁₃ line 267 above it. This relation has already been discussed under the D series above. For Hg he assigns 5814 to F₁(3), 5843 to F₂(3), 5908·68 to F₄(3), 8316·40 to F₁(4), 8409·85 to F₃(4). Now 5843 is double with $dn = 4·8$, corresponding to a displacement δ , and may well be F₂₁ · F₂₂, whilst 5908 is F₃(3). Again, 8316·40 and 8409·85 are separated by 93·45, which is so close to $34·68 + 62·04$ as to indicate that they are F₁(4) and F₃(4) and that F₂(4) has not been observed.

With these allocations VF(3)* = 6939·07 and VF(4) = 4436·66 and the denominators for the lines calculated from the first lines (except CdF₃(4)) are

| Zn. | Cd. | Hg. |
|------------------------|------------------------|------------------------|
| 3·978529 - 287·1 ξ | 3·970387 - 285·3 ξ | 3·975605 - 286·5 ξ |
| | 4·960809 - 556·4 ξ | 4·971938 - 560·3 ξ |

The differences of the mantissæ of the two orders in Cd and Hg are

| Cd. | Hg. |
|--|--|
| 9578 + 271 ξ , $21\delta = 9561$; | 3667 + 274 ξ , $2\frac{1}{2}\delta = 3629$; |

in which the probable variations of ξ are small fractions. In fact, the greatest uncertainties are due to observation errors.

There is not much material to throw light on the origin of the F term here, nor in fact is there evidence that the fundamental lines, or the first lines, of the series are

* On the basis of RITZ'S combining theory PASCHEN gives the following allocations (lines in wave-lengths):—

| | |
|---|---|
| 3011·17 = S ₁ (∞) - VF(3) | 2799·76 = S ₁ (∞) - VF(4) |
| 2642·70 = S ₂ (∞) - VF(3) | 2478·09 = S ₂ (∞) - VF(4) |
| 2524·80 = S ₃ (∞) - VF(3) | 2374·11 = S ₃ (∞) - VF(4) |

There can be little doubt about the correctness of this allocation. Using the value of S₁(∞) in [II.] 40139·55 and the wave numbers 33200·19, 35707·02 of the first lines of each set there results VF(3) = 6939·36, 4432·53, which are practically the same as those found direct.

for $m = 3$. Any lines corresponding to $m = 2$ would have wave numbers about 500, and to $m = 1$ negative wave numbers in the neighbourhood of 16000. Now PASCHEN has noted lines which may be treated as the actual lines in question. They depend on terms $S'(\infty) - VD(2)$ where $S'(\infty)$ is the limit of his singlet series, and of course $VD(2)$ is the $F(\infty)$ of the above. Using sequences for the S' series of the form $\mu = 1 + f$, the limits of the series are

| Zn. | Cd. | Hg. |
|----------|----------|----------|
| 29019·96 | 28843·40 | 30114·33 |

The lines in question are

| Zn. | Cd. | Hg. |
|---------------------|----------|----------|
| $\lambda = 6238·21$ | 6325·40 | 5769·45 |
| $n = 16025·87$ | 15804·98 | 17327·96 |

If these wave numbers be added to $F_2(\infty)$ in each element, there results 29018·62, 28846·14 and 30115·71, *i.e.*, the value of the $S'(\infty)$ above. The corresponding lines for $F_1(\infty)$ do not seem to exist. There is no *a priori* reason to take $F_2(\infty)$ rather than $F_1(\infty)$ for Zn. In Cd, however, the case is settled in favour of F_2 , as the other lines exist, *viz.*, -15526·84, -15793·05, -15804·98, giving the differences 266·21, 11·93 corresponding therefore to the companion series to $D_{13}(2)$, to $D_{13}(2)$ and $D_{12}(2)$, D_{11} not appearing. But in Hg -17327·96, -17264·98, -17223·97, with differences 62·98, 41·01 would seem to assign 17327 to the F_3 term. Nevertheless to get the limit of PASCHEN'S S' series it is necessary to take $F_2(\infty)$.

If these be regarded as the first lines of the F series, the denominators are Zn, $1·943072 - 33·5\xi$; Cd, $1·949840 - 33·9\xi$; Hg, 1·908346. In Hg the line $n = -17121·30$ would seem to stand in a normal relation to the F_1 , as it comes into line with the others as is seen below. With this the apparent limit with F_1 would be 29874·37, giving denominator $1·916040 - 32·0\xi$. The question now is, are these denominators related in any way to those for $m = 3$. The differences of their mantissæ are, using our new Hg line

| Zn. | Cd. | Hg. |
|--------------------------|---------------------|-----------------------|
| $34557 - 254\xi$ | $20547 - 252\xi$ | $59565 - 254·5\xi$ |
| $= 10(3455·7 - 25·4\xi)$ | $2(10273 - 126\xi)$ | $2(29782 - 127·2\xi)$ |
| $= 10\Delta_2$ | $2\Delta_2$ | $2\Delta_2$ |

well within errors, it being also remembered that ξ can only be a fraction. The value of Δ_2 for Hg adopted is the corrected one 29765, from $\delta = 361·85w^2$. This is a striking connection. It shows that the limits for PASCHEN'S singlet series are either $VF(1)$ or are formed from $VF(3)$ by deducting $10\Delta_2$ for Zn, $2\Delta_2$ for Cd, and apparently $2\Delta_2$ for a normal type in Hg which then receives some displacement.

Magnesium.—We are now in a better position to take up the consideration of the place Mg is to occupy in the second group of elements, viz., whether it is allied with the Ca or the Zn sub-groups. In the discussion of MgD (p. 356) there was evidence in favour of either view. If it belongs to the former, then the line $\lambda = 14877$ is $D_1(1)$; if to the latter we have PASCHEN's allocations of 14877 to F(3) and 10812.9 to F(4). Take first the supposition that Mg is analogous to the earths. In this case $F(\infty) = 39751.08 - 6719.95 = 33031.15$, 6719 being the wave number of 14877. If the F series is formed on the type of the Ca set the denominator of the first line will be $2.937300 - 2\Delta_2 = 2.936474$. This gives a line $n = 20312$. No line has been observed sufficiently near to this to be identified with it. In the other case $F(\infty) = D_1(2) = 39751.08 - 26044.99 = 13706.09$. PASCHEN's allocations then give denominators $3.962183 - 283.5\xi$, $4.958710 - 555.7\xi$ with a mantissa-difference $= 3473 + 272\xi$. With $\xi = .9$ this is 3717 or $9\Delta_2$. The value $\xi = .9$ will upset the difference in Table II. between D(2) and the supposed D(1) which in this case does not exist. It still leaves the difference between the denominators of D(2) and $D(3) = 6\Delta_2$. If Mg is completely analogous with the Zn set the combination lines $S(\infty) - VF(3)$, $S(\infty) - VF(4)$ should exist. They should be at $n = 32764.92(.67)$, $+v_1$, $+v_2$, and $35290.72(.87)$, $+v_1$, $+v_2$. Now EDER and VALENTA give two spark lines of weak intensity at 3050.75, 3046.80, and SAUNDERS a weak arc at 3051. The wave numbers in vacuo are 32769.48 and 32811.95 separated by 42.47, which is clearly $v_1 = 40.90$. These are therefore the looked for $S_1(\infty) - VF(3)$, and $S_2(\infty) - VF(3)$, the third $S_3(\infty) - VF(3)$ not having been seen. As to the other set, SAUNDERS has observed a line at 2833 giving $n = 35288.19$ which is clearly $S_1(\infty) - VF(4)$. The existence of these combination lines seems to settle the question in favour of Mg belonging spectroscopically to the Zn group of metals rather than the alkaline earths. It is possible that as a transition element it belongs to both types. Judging from PASCHEN's various readings it might well be that $\lambda = 14877$ is double so that one might be D(1) and the other F(3).

Group III.—In Al and Tl alone have the ultra-red lines been observed, and here the F lines are found in a similar position to those in the Zn groups, and with them RITZ's combinations $S(\infty) - VF(3)$ and $S(\infty) - VP(3)$. Using the values of $D(\infty)$ of [II.] the values of $F(\infty) = VD(2)$ are 15837.92 for Al and 13064.21 with separation 81.98(.24) for $F_2(\infty)$ for Tl. For Aluminium PASCHEN gives $n = 8882.19(.80)$ and 11392.8(3.90) for F(3) and F(4), from which result $VF(3) = 6955.73(.80)$ and $VF(4) = 4445.12(3.90)$. The combination

$$n = 41204.14(3.39) = S_1(\infty) - VF(3) \text{ gives } VF(3) = 6957.32(3.39).$$

For Thallium PASCHEN gives $n = 6118.19(.75)$, 6200.67(.77) for $F_1(3)$, $F_2(3)$ and 8622.47(.37), 8706.78(1.51) for $F_1(4)$, $F_2(4)$. These give separations $82.48 \pm .75 \pm .77$, and $84.31 \pm .37 \pm 1.51$ instead of $81.98 \pm .24$, but the same within limits. He also gives $n = 34526.21(1.79)$, 42321.40(2.69) for $S(\infty) - VF(3)$ and 37022.23(6.85) for

$S_1(\infty) - VF(4)$. The possible errors of the latter, however, are so large that they cannot be used to improve the values found from the direct lines. The limit calculated from $D(\infty)$ of [II.] and $D_{11}(2)$ is 13064.21, but there is some uncertainty owing to the abnormality of $D(2)$ as explained above under the discussion of the D series. The lines $F_1(3)$ and $F_1(4)$ give 6946.02 (.73) for $VF(3)$ and 4441.74 (.37) for $VF(4)$.

In the case of In no ultra-red lines have been observed. In K.R.'s list there appears a doublet $\lambda = 2720.10, 2565.59$, which shows a separation 2213.32, the true doublet separation being about 2212.38. Its relative position in the spectrum compared with that of Al and Tl point it out as the Ritz combination $S(\infty) - VP_1(3)$. K.R. also give a line at $\lambda = 2666.33$ or $n = 37493.77 (2.81)$, which from its position might be $S_1(\infty) - VF(3)$. If so, the value of $VF(3)$ is 6960.99 (2.80) and clearly in line with those of Al and Tl. We shall adopt it provisionally. K.R. mark all these lines as doubtful, but the existence of the doublet separation points to their real existence as In lines. Collecting these give the following:—

| | Al. | In. | Tl. |
|-------------|-----------------------------|----------------------------|----------------------------|
| $VF(3)$. . | $6955.73 + .80p + \xi$ | $6960.99 + 2.80p + \xi$ | $6946.02 + .73p + \xi$ |
| Denom. . . | $3.970842 - 228p - 285\xi$ | $3.969340 - 801p - 285\xi$ | $3.973616 - 215p - 286\xi$ |
| $VF(4)$. . | $4445.12 + 3.90q + \xi$ | | $4441.74 + .37q + \xi$ |
| Denom. . . | $4.967208 - 2177q - 558\xi$ | | $4.969095 - 207q - 559\xi$ |

It is seen that Al and In may be the same within limits. In Tl the uncertainty in $D(2)$ referred to above is such as to raise the limit—and by 19.19—if the explanation there given is correct. A rise of 10 would make the denominator for $m = 3$ the same as for Al and In.

One of the most striking results of this discussion of the F series is the distinct divergence in type between the spectra of the high melting-point elements and those of the low melting point, and at the same time the close resemblance between the individual elements in each division. So close indeed is the resemblance between all the low melting-point elements of Groups II. and III. that the differences between them appear to be almost wholly due to the difference of the limits, or the value of $VD(2)$ and the values of $VF(3)$ are almost the same. To see how closely they agree the denominators to four places of decimals are collected here, and for comparison those of the alkalis.

| | | | | |
|------------|------------|------------|------------|------------|
| Mg 3.9621, | Zn 3.9785, | Cd 3.9703, | Eu ? , | Hg 3.9756, |
| Al 3.9708, | Ga ? , | In 3.9693, | ? , | Tl 3.9736, |
| Na 3.9979, | K 3.9928, | Rb 3.9878, | Ca 3.9773, | ? . |

It is seen how closely the elements in each group agree in spite of a very wide difference in atomic weight, and moreover the mantissæ in all are very close to unity.

It was shown in [I.] that the F series of the alkalis could be represented by a series of the form $m+1-\alpha(1-1/m)$. The same is the case with the Al and Zn groups. As α is so small and varies so little it can scarcely be a function of the atomic weight. The atomic volumes of the elements are much more even and it may be a function of them as is the case with the p -sequence. In fact, in the case of the alkalis, the α are not far from being proportional to v , $2v$, $2v$, $3v$, for the four elements considered, but the data are so inexact and uncertain that it seems not worth while to undertake an exhaustive numerical discussion.

We do not know that the chief lines of these sets are those depending on $m = 3$. If lines exist depending on $m = 2$ they would all be in extremest red, in fact with wave-lengths comparable with those of electro-magnetic waves capable of being experimentally excited, and it is possible that VF(2) might be the same for all low melting-point elements and as for He (see [I.]). For $m = 1$ we should expect the lines of negative wave number in regions which have been observed and in which no such lines have been seen.

The F series in the high melting-point elements, on the contrary, are profoundly influenced by the atomic weight term. Either the lines observed belong to a different type from those of the others, or they are based on a normal type of aggregation which is modified by collateral and other types of displacement due to the splitting up of the typical aggregations, or to a more complex system of new aggregations.

The notation F for these series was adopted in [I.] under the idea that the sequence for it was of a more fundamental nature than the others, and that impression is rather strengthened by the present discussion. It has been seen, for instance, how the limits of PASCHEN'S singlet S' series in the Zn group depend on it. It would be interesting to know whether similar series appear in the alkalis and aluminium group.

The Value of the Oun.

The further knowledge now gained as to ways in which the *oun*—or the Δ —enters in the constitution of spectra, enables a much closer approximation to its actual value to be obtained than was possible from the consideration of the doublet and triplet separations themselves. Amongst the principal aids are (1) the separations themselves, (2) the dependence of the first D denominator on a multiple of Δ , (3) in the triplet elements, on the collateral relations between associated lines, (4) the satellite separations in the D series, (5) the order separations in the D series which show no satellites, (6) collaterals depending on Δ . Of these, Nos. (1) and (4) have the great advantage that the values depend only slightly on the exactness of the limit (the value of ξ), but (4) has the disadvantage that only small multiples of δ are involved, and (1) only Δ itself. There are also various uncertainties which show themselves when a high order of accuracy is desired—chiefly in the elements of the 3rd group. No. (2) has the great advantage of giving considerable multiples of Δ ,

but they depend to a larger extent than (1) and (4) on the exactness of the limit. This inexactness is, however, in general more than compensated by the largeness of the quantities dealt with. Collateral relations also are capable of giving very exact values, but always subject to uncertainty as to the actuality of the relations indicated by the numerical coincidences. This is less apparent in the F series of the high melting-point elements in Group III., where the relations are largely established by analogy between the different elements involved. No. (5) is affected by the exactness of the limit, and is only useful when the separation is taken between the first two orders and it is a considerable multiple of Δ , as, for instance, 117Δ in Al.

For the special purpose of obtaining as exact a value as possible of the ratio δ/w^2 it will be better to exclude from consideration Na, Ga, He, Sc, O, S, and Se. Na is excluded on account of the uncertainty as to whether F. and P.'s interferometer measures of the P(2) lines are to be taken as giving the value of ν for the S and D series, in which a somewhat larger value is indicated by observers using ordinary methods. Ga is omitted on account of its poor spectroscopic data. He because its ν , although very accurately determined, is so small that slight errors are very large proportionate ones. O because ν is small and the observations not so exact, and Sc, S, and Se because their spectra have not been sufficiently discussed. There remain 17 elements for consideration. In the following the case of each element is considered first, with estimates of its possible error. Then using these possible errors as probable errors, the most probable value of δ/w^2 is deduced by least squares. The ratio δ/w^2 is denoted by q .

K. The observations determining ν are very bad. The ν adopted gives $\Delta = 2939$. $D_{12}(2) = 261\Delta$ and gives $\Delta = 2932.27 \pm .130 - .364\xi$, $W = 39.097 \pm .003$, and ξ is about ± 1 . The value of q from this is $361.944 \pm .11$. This is adopted with probable error = .1.

Rb. The only source is from ν , since there is no light from the $D_{12}(2)$ as the satellites are doubtful. The value in Table I. is $361.40 \pm .56$. Probable error taken = .66.

Cs. Table I. gives $361.74 \pm .33$. $D_{11}(2)$ is so close to 17Δ that it seems justifiable to adopt it. The observations seem to show that ξ should be 2 ± 1 in Table II. The denominator is subject also to an observation error of 228. With $W = 132.823 \pm .007$ the consequent value of q is $362.24 \pm .30$, but this value of ξ makes the former value much less. The relation may be a coincidence, as it ought to be near it, and it will therefore be safer to take the first adopted value, $361.74 \pm .33$.

Cu and Ag as in Table I., viz., $361.84 \pm .8$, $361.81 \pm .2$.

Mg. With $\xi = 2$, $d\nu = .06$, $W = 24.362 \pm .002$, $\nu_1 + \nu_2$ gives $q = 362.36 \pm .66$.

The actual first D line has been seen to be uncertain, and in any case Δ_2 is so small that the actual multiple cannot be obtained. There is an order difference of $6\Delta_2$ between $m = 2$ and 3, but the observation errors, and those due to ξ , give Δ with far less exactness than from $\nu_1 + \nu_2$. Value therefore adopted, $362.36 \pm .66$.

Ca. From $\nu_1 + \nu_2$, $\xi = 6$, $d\nu = \cdot 1$, $W = 40\cdot 124 \pm \cdot 005$, $q = 361\cdot 56 \pm \cdot 60$.

The denominator of $D_{13}(2) = 691\Delta_2$ gives $q = 361\cdot 84 \pm \cdot 1$.

From the discussion of CaF, $q = 361\cdot 77 \pm \cdot 2$.

Mantissa difference of CaD (2) and CaD (3) $= 99\Delta_2 = 133542 + 100\xi \pm 28$, $q = 361\cdot 870 \pm 1\cdot 76$, the great uncertainty being due to ξ .

The most reliable appears to be that from $D_{13}(2)$, and is included in the others. Value adopted, $361\cdot 84 \pm \cdot 1$.

Sr. From $\nu_1 + \nu_2$, $\xi = 10$, $d\nu = \cdot 2$, $W = 87\cdot 66 \pm \cdot 03$, $q = 361\cdot 63 \pm \cdot 56$.

The denominator of $D_{13}(2)$ does not appear as a multiple of Δ_2 , whereas that of $D_{12} = 178\Delta_2$. If this is a real relation, $q = 361\cdot 735 \pm \cdot 33$.

From the F collaterals and the denominator of F (2), q cannot be far from $361\cdot 77 \pm \cdot 2$. Adopted value, $361\cdot 77 \pm \cdot 2$.

Ba. From $\nu_1 + \nu_2$, with $\xi = -32$, as modified in Table II., and ± 5 allowed, $d\nu = \cdot 2$ and $W = 137\cdot 43 \pm \cdot 06$, $q = 362\cdot 07 \pm \cdot 53$.

From the $D_{13}(2)$ collateral $= 69\Delta_2$, $q = 361\cdot 968 \pm \cdot 36$ } $361\cdot 913 \pm \cdot 36$.
 From $D_{13}(2)$, as found from the F series, $q = 361\cdot 856 \pm \cdot 36$ }

From the F discussion, $q = 361\cdot 971 \pm \cdot 39$.

The most reliable is probably the mean of those depending on D_{13} . Adopted value, $361\cdot 913 \pm \cdot 4$.

Ra. From $\nu_1 + \nu_2$, $\xi = 1$, $d\nu = \cdot 2$, $W = 226\cdot 4 \pm \cdot 02$, $q = 361\cdot 846 \pm \cdot 66$.

From the F discussion, $q = 361\cdot 94 \pm \cdot 11$, but as there is some uncertainty in the F theory, the limits of error should be greater. Adopted value, $361\cdot 94 \pm \cdot 33$.*

Zn. From $\nu_1 + \nu_2$, with $\xi = 3$, $d\nu = 0$, $W = 64\cdot 40 \pm \cdot 03$, $q = 362\cdot 238 \pm \cdot 36$.

From $D_{13}(2)$, $q = 361\cdot 682 \pm \cdot 47$, and from the F values lying between, $362\cdot 15$ and $361\cdot 87$. Value adopted, $362\cdot 01 \pm \cdot 25$.

Cd. From $\nu_1 + \nu_2$, with $\xi = 2$, $d\nu = \cdot 1$, $W = 112\cdot 3 \pm \cdot 1$, $q = 362\cdot 36 \pm \cdot 66$.

In the $D_{13}(2)$ theory Cd appears to occupy a similar position to that of Sr in the other sub-group, in that the multiple of Δ is carried back to D_{11} or D_{12} . The most accurate is that from $\nu_1 + \nu_2$. Adopted value, $362\cdot 36 \pm \cdot 66$.

Eu. From $\nu_1 + \nu_2$, with $\xi = 10$, $d\nu = 4$, $W = 151\cdot 93 \pm \cdot 03$, $q = 361\cdot 94 \pm \cdot 8$.

From $D_{13}(2)$, $q = 361\cdot 44 \pm \cdot 1$. Adopted value, $361\cdot 94 \pm \cdot 8$.

Hg. From $\nu_1 + \nu_2$. There is some uncertainty as to the ratio of $\Delta_2 : \Delta_1$. $\Delta_2 = 41\delta_2$ best agrees with the transference value from Δ_1 to Δ_2 discussed at the commencement, and it gives a value of $\Delta_2 = 29725\cdot 65$ which is in close agreement with the value found in the F discussion, viz., $29782 - 127\cdot 2\xi$.

* HÖNIGSCHMID ('Sitz. d. k. Akad. Wiss. Wien,' November, 1912) has recently made a careful determination of W , and gives $225\cdot 97$ in place of $226\cdot 4$. This would make the own $363\cdot 11w^2$ —a value quite inadmissible if the spectroscopic data are reliable. Although they are not good, they can hardly be so uncertain as this value of q would indicate. For what it may be worth, the spectroscopic data would seem, therefore, to weigh against the acceptance of the new atomic weight.

The former gives with $\xi = 4$, $d\nu = 0$, $W = 200.3 \pm .3$, $q = 361.423 \pm 1.61$, and the latter 362.09 with a large uncertainty owing to 127.2ξ .

$D_{13}(2)$ gives $q = 361.50 \pm 1.28$. The large possible error is due to the uncertainty in the atomic weight of Hg. Adopted value, 361.50 ± 1.33 .

Al. In Al also there is a large possible variation due to the uncertain atomic weight. $W = 27.10 \pm .05$. From ν , $q = 361.88 \pm 1.5$. There is an order difference 117Δ between $m = 2$ and 3 for the D series (see Table II.). This gives $q = 361.871 \pm 1.30$. The denominator of D (2) gives $q = 361.777 \pm 1.92$, or if there is a satellite $D_{12}(2)$ gives 361.717 ± 1.92 . Adopted value, 361.871 ± 1.33 .

In. From ν , with $\xi = 1$, $d\nu = .25$, $W = 114.8 \pm .5$, $q = 361.947 \pm 3.31$.

From $D_{12}(2)$, if $22\Delta - 16\delta$, $q = 361.871$, but the theory is uncertain. Adopted value, 361.947 ± 3.33 .

Tl. From ν , $q = 362.00 \pm .20$. From $D_{12}(2)$, $q = 361.913 \pm .6$, but with somewhat doubtful theory. Value adopted, $362.00 \pm .20$.

These values for the 17 elements weighted according to the possible errors now give $q = 361.890$. This is the same as our first approximate value, but its probable error is much less. If the determination of the value depended only on questions of errors of calculation and of observation in spectral and atomic weight data, the above number would probably be extremely close to the actual one. It must be remembered, however, that our theory of the constitution is not yet complete. For instance, in [II.] it was seen that the supposition that N was not constant for the p -sequence, but that the value for the first line was slightly larger explained the introduction of a term in the denominator. A similar explanation might explain the fact that the value of q appears to deviate from the mean by about the same amount in each group of elements, and if it were justified, the value of q calculated as above would receive a slight modification. I believe it will be found ultimately that the true value will lie within the limits given by $361.890 \pm .05$ or $90.4725 \pm .0125$.

If the existence of the ω as a definite proportion of the (atomic weight)² be considered as established, the best and most direct method of determining the value of the factor q would be from the discussion of an element in which the spectroscopic data are good and in which the atomic weight has been determined with great accuracy. For this purpose we naturally turn to silver. Regarded as the ultimate standard of atomic weight determinations, no error in the atomic weight enters—the value of q is determined in terms of $W = 107.88$. Moreover its separation is large, so that any error of measurement is a small fraction of its total value, and in addition the actual error is extremely small. It is therefore tantalising to find that the lines, D (2) excepted, are not susceptible of such exact measures as in many others, that the typical series are not well developed, and that in fact there may be a doubt whether the lines generally accepted as the P, S, D series follow laws altogether analogous to those in other groups. In KAYSER and RUNGE'S measures four lines are assigned to $D_{11}(2-5)$ and three to $D_2(2-4)$, the possible errors for D_{21} being much less

than for D_{11} . Using $D_{21-\nu}$ for D_{12} and calculating the formula constants from the first three, there results for the D_{12} series

$$n = 30644.60 - N \left/ \left(m + .994354 - \frac{.034384}{m} \right)^2 \right.,$$

with the large possible variation in $D(\infty)$ of $\xi = 12.23$. Using this value of the limit and calculating the formula for D_{11} , the line $D_{11}(5)$ is reproduced with $O-C = .22$, O being $.5$. If, however, the S lines be used with $\mu = f$ the limit comes to $S(\infty) = 30614.60 \pm 3.60$ and the fourth line is reproduced within limits. $S(\infty)$ and $D(\infty)$ cannot be the same within error limits. If $\mu = 1+f$, $S(\infty) = 30633.47 \pm 3$, and the limits can be the same, viz., with $\xi = -9.73 \pm 2.50$ on $D(\infty)$, but μ cannot be $1+f$ if the doublet usually assigned to P belongs really to a P series. I had intended to supplement the direct determination of Δ from ν by a discussion of collaterals, of which both Ag and Cu afford a large number. The doubt however about the form $\mu = 1+f$, and the presence of the numerous collaterals, gives a suspicion that the series are related to the F series with limits based on the typical $S(\infty)$, that they are analogous to the F terms in the high melting-point elements of Group II., and that the doublet usually allocated to the P series is really analogous to the F triplets with negative wave numbers found in Ca and Sr . That discussion is therefore held back for the present.* But certain points not open to doubt and forming a portion of the work of the accurate determination command a place here.

The $D(2)$ lines are sharp. F and P have measured the lines $D_{11}(2)$ and $D_{21}(2)$ with their interferometer. Their measures give a separation of $900.3419 \pm .0070$. In order to get full advantage of their accuracy, and to avoid the uncertainty due to the last significant figure it is necessary to use logarithmic tables with more than 7 figures. This has been done on the supposition that F and P 's errors are not larger than $.001 \text{ \AA.U.}$, *i.e.*, unity in the seventh significant figure. The old measures are sufficient to show with certainty that the satellite difference is $23\delta_1$, and the old approximation to Δ will give $23\delta_1$ with an inappreciable error, whence D_{12} can be found. Taking $D(\infty) = 30644.6000 + \xi$ the mantissa of $D_{11}(2) = 5465.671$ is $979596.44 - 120.59\xi$ and $23\delta_1 = 2421.18 - .15\xi$. Hence the mantissa of D_{12} is the difference or $977175.26 - 120.44\xi$. VD_{12} calculated from this is $12373.6789 + 1.0045\xi$, giving with VD_{21} the value $\nu = 920.4431 + 0.045\xi$ in which the correction for ξ is only effective if $\xi > 10$. The value of Δ calculated from this is $27786.80 - 1.473\xi \pm .20$, in which the uncertainty of $.20$ is due to the uncertainty $.001$ in λ . This value is 4 less than that of Table I. obtained by supposing $K.R.$'s values for D_{12} and D_{21} had no errors. It gives $\delta = (361.754 \pm .0026 - .0152\xi)w^2$. With the mean value $\xi = -9.75$ suggested above this becomes $\delta = (361.902 \pm .0026)w^2$.

The foregoing is interesting also because it shows how the application of the laws developed in the present discussion can help towards more accurate determinations of

* The value obtained for q from the collaterals was $361.708 \pm .0026 - 0.169\xi$, which with $\xi = -10$, as indicated in the text, gives a value surprisingly close to that deduced from all the elements combined.

quantities involved. For instance, it has enabled us to obtain a value of ν correct to about a unit in the sixth significant figure. In the case of Au, the knowledge is still more fragmentary than in Ag and the value of Δ has not been determined. By the application of our new laws, however, it is possible to obtain a good deal of information based on evidence of weight, and it will be interesting to consider it shortly here. Although the spectrum of Au shows many analogies with those of Cu and Ag, no lines have been assigned to the S or D series. There is a strong doublet in the ultra-violet 2676.05, 2428.06 ($\nu = 3815.28$) analogous to the lines allocated to the P series in Cu and Ag. There is only one other doublet in K.R.'s list with the same separation, viz., 6278.37, 5064.75 ($\nu = 3815.54$). This is clearly analogous to the doublets 5782.30, 5700.39 in Cu and 5545.86, 5276.4 in Ag, which have the respective doublet separations but which do not belong to the S or D series. E and H however give an arc line at 4811.81, which gives a separation of 3815.57 with K.R.'s line at 4065.22. This has the appearance of a D set, D_{11} being at 4792.79 with a satellite separation of 82.47. But if so it is quite out of step with the progression of the D_{12} lines for Cu and Ag, viz., 5220 (Cu), 5471 (Ag). But 5837.64 gives with the above 4792.79 a separation 3733.43 the same as that between 4792 and 4065, and they are in step with Cu and Ag as $D_{11}(2)$ and $D_{21}(2)$, the fainter satellite D_{12} being unobserved. This would seem the more probable allocation. In any case, the curious doubling of a D type would have to be explained. There is, however, here not sufficient data to determine the limits, or the other formulæ constants or the value of Δ . But it is possible to arrive at a probable estimate by the following considerations. The limit $D(\infty)$ will probably be in step with those of Cu and Ag, viz., 31515, 30644, *i.e.*, will be in the neighbourhood of 30000. Now Δ must give $\nu = 3815.54$ and must itself be a multiple of the δ , in fact if it is similar to Cu and Ag of δ_4 . Now $W = 197.20$ with an uncertainty of a few units in the second decimal place. The ratio $q = 361.80^* + y$, where y is probably not greater than 1 in the first decimal place and it will be regarded as a correction on the .8. From this it follows that $\delta = 1406.930 \pm .097 + .38y$. The uncertainty .097 due to the uncertainty in W produces so small an effect that it may be neglected here. Now Δ must be a multiple of δ and must give with the proper value of $D(\infty)$, $\nu = 3815.54 + .30s$, .30 being the maximum error of ν and therefore s between ± 1 . This condition gives the following sets of possible limits in the neighbourhood of $D(\infty) = 30,000$:—

| | | |
|-------|---------------------------|--------------------------|
| | $30819.15 + 1.57s - 6y$ | with $\Delta = 76\delta$ |
| about | 30542 | ,, 77 δ |
| ,, | 30266 | ,, 78 δ |
| ,, | 29994 | ,, 79 δ |
| ,, | 29724 | ,, 80 δ |
| | $29465.18 + 1.45s - 5.7y$ | ,, 81 δ |

* The actual calculations were made before the last most probable 361.890 was obtained, but nothing is to be gained by recalculating to it.

If now the lines 5837·64, 4792·79 be taken as $D_{11}(2)$, $D_{21}(2)$, their wave numbers are 17125·54 (·14), 20858·97 (·22), giving for the wave number of $D_{12}(2)$, or $D_{21}-\nu$, the value 17043·43 ($\cdot 22q - \cdot 30s$). In this $\cdot 22q$ is the possible observation error in $D_{21}(2)$. The satellite separation of 82·11 must therefore be caused by a denominator difference which is also a multiple of δ_1 . If this be tested, it is found at once that only the first and last of the above set can satisfy this condition, 30819 taking $24\delta_1$ or 6δ , and 29465 taking $28\delta_1$ or 7δ . The corresponding values for Cu and Ag are both $23\delta_1$. The differences between the values calculated from the lines and from the multiples of δ_1 are (p between ± 1 giving the observation error in $D_{11}(2)$).

$$38\cdot 4 + 28s + 3\cdot 0y + 14p - 22q \text{ with } 24\delta_1 = 8441$$

$$20 + 34\cdot 3s + 4y + 17p - 26q \quad ,, \quad 28\delta_1 = 9869.$$

It is clear that either can easily be made to vanish well within possible errors, more especially the latter. The limit 30819 is higher than that of Ag instead of lower as might be inferred from the fact that the limit of Ag is lower than that of Cu. The limit 29465 is 1179 below that of Ag, which is itself 931 below that of Cu. This seems a probable order of magnitude, especially when it is remembered that there is a gap in the Periodic Table between Ag and Au. But there is further evidence in favour of the latter. If the lines 6278·37, 5064·75 are collaterals of $D(2)$ as the corresponding lines in Cu and Ag appear to be, 6278·37 should be $D_{11}(2)(x\delta_1)$. With the limit 30819 this cannot possibly be the case. The own $\delta_1 = 351$ is so large that there can be no doubt. If however the limit is 29465, the line is $D_{11}(2)(\Delta + 15\frac{1}{4}\delta)$. Further, with neither limit is the mantissa of $D(2)$ a multiple of δ , and as this is also not the case with Ag or Cu, it may be regarded that in this group either these lines are not of the D type, or possibly like the high melting-point elements of Group II. the first lines correspond to $m = 1$ and not $m = 2$. The actual values of the denominators as found are so close to the same value for all three elements as to suggest the existence of a group constant. If the limit 29465 is used the denominators are as given below, and as is seen they differ from such a constant by very small multiples of δ .

| | Cu. | Ag. | Au. |
|---------------|----------------------------|----------------------------|----------------------------|
| Density . . . | 978276 (21) | 977162 (19) | 971409 (26) |
| | $146 = \delta$ | $1263 = 3\delta$ | $7034 = 5\delta$ |
| | <hr style="width: 100%;"/> | <hr style="width: 100%;"/> | <hr style="width: 100%;"/> |
| | 978422 (21) | 978425 (19) | 978443 (26) |

or say a group constant 978430. Whether this apparent equality corresponds to a real relation or not must be left for further evidence. In any case a limit $D(\infty) = 30819$ would throw this relation quite out.

As a final result the evidence would seem conclusive that $D(\infty)$ for Au is 29465.18 ± 7 , that $\Delta = 81\delta = 113961 \pm 31.5y$, and that the satellite separation is produced by $28\delta_1$.

Summary.

It must be confessed that much of the foregoing discussion is of a problematical nature, and that, in fact, some of the suggestions offered are incompatible with one another. This is no objection in a preliminary search for general principles, as the raising of questions is only next in importance to answering them. Nevertheless, some results appear to be well established and others to have considerable evidence in their favour. Amongst the first are—

(1) The dependence of the spectrum of an element on its own, a quantity proportional to the square of its atomic weight and which probably does not differ from $\delta_1 = 90.4725w^2$ by more than $.013w^2$ where w denotes one-hundredth of the atomic weight;

(2) The direct dependence of the ordinary doublet and triplet separations on multiples of the own;

(3) A similar dependence of the satellite separations in the Diffuse—or the 1st associated—series on multiples of the same quantity;

(4) The existence of collateral displacement, whereby new lines are formed by the addition or subtraction of multiples of the own. Until, however, the laws which govern the formation of collaterals are more fully known, it is not safe to assume that any displacement indicated by mere numerical coincidence corresponds to the physical change such collateral indicates. Nevertheless, many cases of clear displacement of this kind, involving considerable multiples of Δ , especially in the F series, are given which serve to give more accurate values of the own.

The conditions which govern the various multiples of the own which enter in the various separations have not been determined. It is probable, however, that the multiple for the doublet, or first two of a triplet, in the two sub-groups of the n^{th} group of elements contain $2n+1$ and $2n+2$ respectively as factors.

It is probable that the mantissa of the normal first line of the Diffuse series, the last satellite, when such exists, being considered as the normal, is a multiple of Δ , and it is possible that its magnitude has some general relation of approximation to that of the corresponding F series, which again may depend directly on a group constant.

It is possible that the wave numbers of the lines in the Diffuse and F series may not depend directly on a mathematical function of the order m of the line, and it is probable that this is the case when there are no satellites, the differences now being multiples of the Δ themselves.

In the discussion of the material it has been attempted to keep the mind as free as

possible from any preconceived theories as to the origin of the vibrations which give the lines. The aim has been to discover relations, which it must be the object of theories to explain. Nevertheless, the way in which multiples of a quantity depending directly on the element enter, and indeed multiples of these multiples, irresistibly suggests that each line is due to a special configuration built up of aggregates of the same kind. Thus, in the Zn group appear multiples of $6\delta_1$, in Mg, of $5\delta_1$, &c. These smaller aggregates peculiar to a group then appear to enter like radicals into more complex aggregates, *e.g.*, in Zn $\Delta_1 = 31\delta_6$, $\Delta_2 = 15\delta_6$, and again, multiples of Δ_2 occur in collaterals. In cases, a certain aggregate, normally to be expected, appears to be affected with instability, a certain number of electrons are expelled or added and we get a stable collateral. In the case of rich spectra and of spark spectra, a very large proportion of the lines appear to be collaterally connected. It suggests systems in which a greater freedom of aggregation is permissible. But there is another way in which the matter may be looked at. The actual multiples may be determined by the number of electrons taking part in the vibrations, and the quantity enters into the formula as the product of this number by a fundamental quantity of the atom. But it is difficult to see how this quantity should depend on the square of the mass. It would almost look as if the gravitational pressure of two atoms always at the same distance produced some change in the configuration of the surrounding æther proportional to the pressure, and that the vibrations were conditioned by this change and by definite numbers of electrons. In any case, the existence of the line, and the extent in which its influence is shown in a spectrum, point to the conclusion that the positive atom plays an essential part in at least those vibrations emitted which are slow enough for us to observe.

APPENDIX I.

The Value of Δ in Scandium.

The value of Δ as a multiple of δ in Scandium is of importance in connection with the evidence as to the curious relation, that the Δ 's of the first elements of the two sub-groups in the n^{th} group are multiples of $(2n+1)\delta_1$ and $(2n+2)\delta_1$. The lines in the visible part have been measured by FOWLER,* and lines both in visible and ultra-violet by EXNER and HASHEK.†

I do not altogether feel full confidence in the allocation suggested below, but it gives related series, even if not the typical ones, and so will serve to determine Δ . The doublet separation is $320 \pm$ a small fraction. There are over 34 doublets with this separation—two, 3613·96, 3572·71 and 3576·52, 3535·88 containing some of the strongest lines in the spectrum. The lines suggested for the S series appear to show

* 'Phil. Trans.,' 209, p. 66.

† 'Spektren der Elemente: Bogenspektren.'

satellites in the first two sets. Further, it appears that the P series take the *s*-sequence and the S series the *p*-sequence as is the rule outside the alkalis.

The P Lines.

(Figures in brackets give intensities.)

| <i>m.</i> | P ₁ . | P ₂ . | <i>n</i> ₁ . | | <i>n</i> ₂ . |
|-----------|------------------|------------------|-------------------------|--------------|-------------------------|
| 4. | (5) 5717·51 | (0) 5721·20 | 17485·35 | 11·27 | 17474·08 |
| 5. | (5) 5258·49 | | 19011·70 | | |
| 6. | (2) 5021·67 | | 19908·26 | | |
| 7. | (1) 4880·90 | | 20482·40 | | |
| 8. | (2) 4791·69 | | 20863·72 | | |
| 9. | (2) 4728·95 | | 21140·54 | | |
| 10. | (0) 4682·16 | | 21351·78 | | |

S Series.

| | | | | | |
|----|--------------|-------------|--------------|---------------|----------|
| 1. | (6) 6413·54 | (3) 6284·66 | 15587·78 | 319·65 | 15907·43 |
| | | | 84·35 | | |
| | (6) 6379·02 | | 15672·13 | | |
| 2. | (15) 3646·46 | (1b) 3603·1 | 27423·71 | 322·39 | 27746·10 |
| | | | 25·81 | | |
| | (50) 3642·93 | | 27449·52 | | |
| 3. | (2) 3139·98 | (1) 3108·70 | 31838·31 | 320·37 | 32158·68 |

Parallel S Series.

| | | | | | |
|----|-------------|-------------|--------------|---------------|----------|
| 1. | (3) 5146·43 | (0) 5323·94 | 18457·31 | 320·65 | 18777·96 |
| | | | 82·60 | | |
| | (6) 5392·30 | | 18539·91 | | |
| 2. | | (2) 3273·76 | | | 30537·33 |

The S Series.—For a reason to be seen shortly, it is necessary to regard S₁₁(1), S₁₁(2), S₁(3) as the typical series, S₁(3) as not displaced, but the doublets corresponding to 1 and 2 are displaced collaterally to S₁₂. In other words, we have to do with bodily displacements of the first two doublets and not true satellites. The mean of the doublets gives $\nu = 320\cdot80$, and the formula calculated from the three lines is

$$37949\cdot90 - N \left/ \left(m + 1\cdot244902 - \frac{0\cdot026104}{m} \right)^2 \right.$$

With the value of ν above the value of Δ calculates with this limit to $7140 = 203\delta_2$ with $\delta = 70\cdot34$. The denominator differences of S_{11} and S_{12} for $m = 1$ and 2 are respectively 4188 and 3964 , *i.e.*, close to $59\delta = 4150$ and $57\delta = 4010$, with errors in $d\lambda$ of $\cdot31$ and 0 , divided between the two sets of lines. It is possible they may be the same within limits of error (59δ), when the value of $d\lambda$ in the second would be $-\cdot16$.

The formula for P , calculated from the first three lines, is

$$n = 22281\cdot97 - N \left/ \left(m + \cdot828585 - \frac{\cdot187372}{m} \right)^2 \right.$$

This formula gives the following values of $O-C$ for the lines for $m = 7, 8, 9, 10$, *viz.*, $-\cdot55, \cdot85, \cdot26, -1\cdot86$. If the denominator be treated in the same way as Al ,* *i.e.*, deducting the group constant $\cdot043761$, it may be put into the form $m - \cdot043761 + \cdot872346 \left(1 - \frac{\cdot21480}{m} \right)$, which reproduces the $\cdot215$ constant. Also $VS(1) = 22277\cdot80 = P(\infty)$ within error limits.

If $S_1(3)$ had been taken as $S_{12}(3)$ this would not have been the case. But $VP(1)$ extrapolates to $40717\cdot20$ with a denominator $1\cdot641213$, whilst $S(\infty) = 39749\cdot90$ with a denominator $1\cdot699998$, and they cannot be the same even approximately if the typical formula holds. The extrapolated value of $VP(1)$ requires $\Delta = 6428$ to give $\nu = 320\cdot8$ or 91δ , again giving a multiple of $7\delta_1$ and at the same time more in line with other elements as being a multiple of δ itself, and a multiple more in step with them. It points to the likelihood that the series chosen for S is a parallel series to the true S , *i.e.*, the $VS(m)$ is correct. If so, using the values of $VS(1, 2)$ with $S(\infty) =$ the extrapolated limit 40717 , we should expect doublets with the first lines at 18440 and 30217 . There is a doublet at $18457\cdot31$, no line observed at 30217 , but the doublet companion expected at 30537 is found at $30537\cdot33$. Also 18457 appears as a satellite to a stronger line $18539\cdot91$ in a corresponding position $82\cdot60$ a-head. The second set of lines above is, therefore, probably the true S series, the first being a parallel one. With limit $40717\cdot20$ and $\nu = 319\cdot45$, the mean of all the doublets, the value for Δ is $6404 = 91\delta$ with $\delta = 361\cdot89w^2$. The value of $361\cdot89$ is subject to considerable uncertainty owing to uncertainties in the limit value and the atomic weight, and its agreement with the final estimate for the *oun* is a mere coincidence. The spectrum of Sc is a most interesting one, but its discussion must be postponed. The object of touching upon it here is to obtain some indication of the nature of its *oun* as Sc occupies the first place in its sub-group. It would clearly appear that the multiple of the *oun* in Δ contains 7 as a factor, *viz.*, $13 \times 7\delta = 52 \times 7\delta_1$.

The separation of $P_1(4)$ and $P_2(4)$ is $11\cdot26$, corresponding to a denominator difference of $5607 = 80\delta$. This is in fair agreement with the case of other P series in which the differences for orders below the first are about $\cdot8\Delta$.

* [II., p. 46.]

APPENDIX II.

The D Series.

| | | Na. | | | K. | |
|------|-------------|----------|--------|--------------|---------------|----------|
| S. | (2) 8196·1 | 8184·5 | P. | (2) 11771·73 | 11689·76 | |
| K.R. | 5688·26 | 5682·90 | S. | 6966·3 | K.R. 6938·8 | |
| „ | 4983·58 | 4979·30 | K.R. | 5832·23 | 5812·54 | |
| „ | 4669·4 | 4665·2 | „ | 5359·88 | 5343·35 | |
| „ | 4500·0 | 4494·3 | „ | 5112·68 | 5097·75 | |
| Z. | 4393·5 | 4390·1 | „ | 4965·5 | 4952·2 | |
| „ | 4324·5 | 4321·3 | S. | 4871·3 | S. 4856·8 | |
| „ | 4276·7 | 4273·6 | L.D. | 4808·8 | L.D. 4796·8 | |
| „ | 4241·8 | 4239·0 | „ | 4759·8 | | |
| „ | 4215·8 | 4213·0 | | | | |
| „ | 4195·7 | 4192·8 | | | | |
| „ | 4180·2 | 4177·2 | | | | |
| „ | | 4168 | | | | |
| | | Rb. | | Cs. | | |
| RL. | (2) 15290·3 | 14754·0 | P. | (2) 36127·7 | } 30099·9 | |
| S. | 7759·5 | } 7619·2 | | 34892·5 | | |
| „ | 7757·9 | | | „ | 9208·3 | } 8761·5 |
| | 6298·8 | K.R. | 6206·7 | „ | 9172·5 | |
| K.R. | 5724·41 | 5648·18 | S. | 6983·8 | } K.R. 6723·6 | |
| „ | 5431·83 | 5362·94 | K.R. | 6973·9 | | |
| RE. | 5260·51 | 5195·76 | RE. | 6217·6 | } „ 6010·59 | |
| „ | 5151·20 | 5089·25 | K.R. | 6213·4 | | |
| „ | 5076·3 | 5017 | RE. | 5847·86 | } „ 5664·14 | |
| „ | 5023 | K.H. | 4963 | „ | | 5845·31 |
| „ | 4983 | „ | 4926 | „ | 5635·44 | 5466·1 |
| K.H. | 4953 | 4892 | „ | 5503·1 | 5341·15 | |
| | | | „ | 5414·4 | 5256·96 | |
| | | | „ | 5351 | 5199 | |
| | | | „ | 5304 | 5154 | |
| | | | | | H. 5118 | |

| Mg. | | | Ca. | | |
|-------------|---------|---------|-------------|------------|---------|
| (2) 3838·44 | 3832·46 | 3829·51 | (2) 19917·5 | 19507·1 | 19310·6 |
| 3097·06 | 3093·14 | 3091·18 | 19864·6 | 19452·9 | |
| 2852·22 ? | 2848·53 | 2846·91 | 19777·4 | | |
| 2736·84 | 2733·80 | 2732·35 | 4456·81 | 4435·86 | 4425·61 |
| 2672·90 | 2669·84 | 2668·26 | 4456·08 | 4435·13 | |
| 2633·13 | 2630·52 | | 4454·97 | | |
| 2605·4 ? | | | 3644·86 | 3631·10 | 3624·15 |
| | | | 3644·50 | 3630·83 | |
| | | | 3361·92 | 3350·22 | 3344·49 |
| | | | 3225·74 | 3215·15 | 3209·68 |
| | | | 3150·85 | 3140·91 | 3136·09 |
| | | | 3101·87 | | |
| Sr. | | | Ba. | | |
| (2) 30110·7 | 27356·2 | 26024·5 | | | |
| 29225·9 | 26915·4 | | | | |
| 4971·85 | 4876·35 | 4832·23 | (3) 5819·29 | S. 5536·07 | 5424·82 |
| 4968·11 | 4872·66 | | 5800·48 | 5519·37 | |
| 4962·45 | | | 5777·84 | | |
| 4033·25 | 3970·15 | 3940·91 | 4506·11 | 4333·04 | 4264·45 |
| 4032·51 | 3969·42 | | 4493·82 | 4323·15 | |
| 4030·45 | | | 4489·50 | | |
| | 3653·90 | 3629·15 | | S. 3947·6 | 3889·45 |
| 3705·88 | 3653·32 | 3628·62 | S. 4087·53 | „ 3946·6 | |
| 3547·92 | 3499·40 | 3477·33 | „ 4084·94 | | |
| 3457·70 | 3411·62 | 3390·09 | „ 3895·2 | „ 3767·5 | |
| 3400·39 | | | „ 3787 | | |
| Zn. | | | Cd. | | |
| (2) 3346·04 | 3303·03 | 3282·42 | (2) 3649·74 | 3500·09 | 3403·74 |
| 3345·62 | 3302·67 | | 3614·58 | 3467·76 | |
| 3345·13 | | | 3613·04 | 3466·33 | |
| | 2771·05 | 2756·53 | 3610·66 | | |
| 2801·17 | 2770·94 | | 3005·53 | 2903·24 | 2837·01 |
| 2801·00 | | | 2982·01 | 2881·34 | |
| 2608·65 | 2582·57 | 2570·00 | 2981·46 | 2880·88 | |
| 2516·00 | 2491·67 | 2479·85 | 2980·75 | | |

| Zn (continued). | | | Cd (continued). | | | |
|-----------------|-----------|---------|-----------------|------------|------------|----------|
| 2463·47 | 2439·94 | | 2764·29 | 2677·65 | 2639·63 | |
| 2430·74 | 2407·98 | | 2763·99 | | | |
| | | | 2660·45 | 2580·33 | 2544·84 | |
| | | | 2601·99 | 2525·57 | | |
| Eu. | | | Hg. | | | |
| (2) 3637·84 | } 3320·03 | 3212·89 | (2) 3680·74 | } 3144·61 | } 2967·64 | |
| | | | 3663·46 | | | 3131·94 |
| 3638·22 | } 3313·46 | | 3663·05 | } 3131·68 | } | |
| 3629·94 | | | 3654·94 | | | 3125·78 |
| 3622·70 | | | 3650·31 | | | |
| 3004·9 | } | 2708·91 | 3027·62 | } 2655·29 | } 2536·72 | |
| 3001·48 | | | 3025·79 | | | 2653·89 |
| | 2596·49 | | 3023·71 | } 2652·20 | } | |
| | | | 3021·64 | | | |
| 2683·29 | } | | 2806·844 | } 2483·871 | } 2380·061 | |
| 2682·72 | | | 2455·03 | | | |
| | } 2423·03 | | 2804·521 | } 2482·072 | } | |
| | | | 2564·27 | | | 2401·15 |
| | 2387·41 | | 2700·92 | } 2400·570 | } 2302·165 | |
| | | | 2699·503 | | | 2399·812 |
| | | | 2698·885 | 2399·435 | | |
| | | | 2639·92 | 2352·647 | 2258·871 | |
| | | | 2603·10 | 2323·0 | | |
| | | | 2578·34 | | | |
| | | | 2561·15 | | | |
| | | | 2548·51 | | | |
| | | | | | | |
| | | | 2531·74 | | | |
| | | | 2525·90 | | | |
| | | | 2521·27 | | | |
| | | | 2517·57 | | | |
| | | | 2514·48 | | | |

(see [II., p. 60] for details)

| Al. | | Ga. | |
|----------------------------|---------|----------------------------|-----------|
| (2) 3092·95 } 3092·84 } | 3082·27 | See Part II., p. 71. | |
| 2575·49 } 2575·20 } | 2568·08 | | |
| 2373·45 } 2373·23 } | 2367·16 | | |
| 2269·20 | 2263·52 | | |
| 2210·15 | 2204·73 | | |
| 2174·13 | 2168·87 | | |
| 2150·69 | 2145·48 | | |
| 2134·81 | 2129·52 | | |
| 2123·44 | 2118·58 | | |
| In. | | Tl. | |
| (2) 3258·66 } 3256·17 } | 3039·46 | (2) 3529·58 } 3519·39 } | 2767·97 |
| 2714·05 } 2710·38 } | 2560·25 | 2921·63 } 2918·43 } | 2379·66 |
| 2523·08 } 2521·45 } | 2389·64 | 2710·77 } 2709·33 } | 2237·91 |
| 2430·8 } 2429·76 } | 2306·8 | 2609·86 } 2609·08 } | 2168·68 |
| 2379·74 | 2260·6 | 2553·07 } 2552·62 } | 2129·39 |
| | 2230·9 | 2517·50 | C. 2105·1 |
| | 2211·2 | 2494·00 | „ 2088·8 |
| | 2197·5 | 2477·58 | „ 2077·3 |
| | 2187·5 | 2465·54 | „ 2069·2 |
| | 2180·0 | 2456·53 | „ 2062·3 |
| | | 2449·57 | „ 2057·3 |
| | | 2444·00 | „ 2053·9 |
| | | 2439·58 | „ 2050·6 |
| | | | „ 2048·4 |

| | | O. | | | |
|--------|----------|----------|----------|--|----------------|
| | | D'''. | | | D''. |
| P. (2) | 9264·28 | | | | P. (2) 11287·0 |
| R.P. | 6158·415 | 6156·993 | 6165·198 | | R.P. 7002·48 |
| „ | 5330·835 | 5329·774 | 5329·162 | | „ 5958·75* |
| „ | 4968·94 | 4968·04 | 4967·58 | | „ 5512·92 |
| „ | 4773·94 | 4773·07 | 4772·72 | | „ 5130·70 |
| „ | 4655·54 | 4654·74 | 4654·41 | | „ 4973·05 |
| „ | 4577·84 | | 4576·97 | | |
| „ | 4523·70 | | 4522·95 | | |

New D.

| | | | |
|----------|---------|---------|---------|
| R.P. (3) | 6264·78 | 6261·68 | 6256·81 |
| | 5410·97 | 5408·80 | 5405·08 |
| | 5037·34 | | |

| S. | | | Se. | | | | |
|----------|---------|---------|---------|----------|-----------|---------|------------|
| R.P. (4) | 6757·40 | 6749·06 | 6743·92 | R.P. (4) | 7062 | 7014·25 | } 6990·96* |
| „ | 6052·97 | 6046·23 | 6042·17 | | | 7010·86 | |
| „ | 5706·44 | 5700·58 | 5697·02 | „ | { 6325·81 | 6284·51 | |
| „ | 5507·20 | 5501·78 | 5498·38 | „ | { 6325·4 | 6284·19 | 6266·36 |
| „ | 5381·19 | 5375·98 | 5372·82 | „ | { 5962·08 | 5925·31 | |
| „ | 5295·86 | 5290·89 | 5287·88 | „ | { 5961·7 | 5925·13 | 5909·49 |
| | | | | | { 5753·52 | 5718·5 | |
| | | | | | { 5752·31 | 5718·28 | 5703·86 |
| | | | | | 5618·05 | | |
| | | | | | 5528·64 | 5497·06 | |
| | | | | | 5464·82 | | |

* Double.

The F Series.

| Na. | | | K. | | |
|------|---------|-----------------|------|-----------|-----------------|
| | | | P. | 84520 | ? |
| | P. | 18459·5 | „ | 15165·8 | |
| | „ | 12677·6 | „ | 11028·0 | |
| | | | BN. | 9590 | |
| | | | „ | 8908 | |
| | | | „ | 8500 | |
| Rb. | | | Cs. | | |
| | P. | 46960 ? | P. | 30099·9 ? | 29318·3 ? |
| | RL. | 13443·7 | RL. | 10124·0 | 10025·5 |
| | „ | 10081·9 | „ | 8083·1 | } 8020·6 |
| | BN. | 8872 | „ | 8080·9 | |
| | „ | 8271 | S. | 7280·5 | 7228·8 |
| | | | „ | 6872·6 | 6826·9 |
| | | | „ | 6630·5 | 6588 |
| | | | „ | 6475 | 6434 |
| Ca. | | | Sr. | | |
| K.R. | 6169·87 | 6161·60 | L. | { 6754·21 | 6708·10 |
| „ | 6169·36 | | „ | { | 6644·05 6616·92 |
| Bs. | 4586·12 | 4581·66 4578·81 | K.R. | { | 4869·41 4855·27 |
| „ | 4098·66 | 4095·05 4092·76 | E.H. | { 4892·90 | K.R. 4868·92 |
| „ | 3875·85 | 3872·60 3870·57 | K.R. | { 4892·20 | |
| „ | 3753·56 | 3750·40 3748·39 | „ | 4338·00 | 4319·39 4308·49 |
| „ | 3678·46 | 3675·53 3673·49 | F. | 4087·67 | 4071·01 4061·21 |
| | | | „ | 3950·96 | 3935·33 3926·27 |
| | | | S. | 3867·3 | |

Analogous Sets in Ca and Sr.

| | | | | | | | |
|------|---------|---------|---------|------|---------|---------|---------|
| K.R. | 5601·51 | 5594·64 | 5590·30 | K.R. | 5535·01 | 5504·48 | 5486·37 |
| „ | 5588·96 | 5582·16 | | „ | 5481·15 | 5451·08 | |
| „ | 5270·45 | 5264·46 | 5260·58 | „ | 5257·12 | 5229·52 | 5213·23 |

| | Ba. | | Ra. | |
|------|------------------------|------------------------|----------------|---------------------|
| HR. | 7637·47 | 7488·38 | | |
| L. | 7420·96 | HR. 7280·58 | L. 7197·99 | |
| HR. | 7417·80 | | | |
| HL. | 5349·71 | K.R. 5277·84 | R. & P. 5778·5 | 5553·81 |
| K.R. | 4691·74 | 4636·80 | 4605·11 | 4444·4 |
| „ | 4402·75 ⁽¹⁾ | 4350·49 | 4333·04* | { 4682·359 4533·327 |
| „ | 4224·11 ⁽²⁾ | 4179·57 ⁽³⁾ | 4166·24 | |

⁽¹⁾ F₁₂ (5) (Δ₂).⁽²⁾ F₁ (6) (9Δ₂).⁽³⁾ F₃ (6) (8Δ₂).* D₂₂ (4) and F₃ (5) not resolved.

| Mg. | | Zn. | |
|-----|---------|-----|---------|
| P. | 14877·1 | P. | 16498·6 |
| „ | 10812·9 | | 16490·3 |
| | | | 16483·7 |

| Cd. | | | Hg. | | |
|-----|---------|---------|---------|----|----------|
| P. | 16482·2 | 16433·8 | 16401·5 | P. | 17195 |
| „ | | | 11630·8 | „ | 12021·28 |
| | | | | | 16919·84 |
| | | | | | 11887·71 |

| Al. | | Tl. | |
|-----|---------|-----|---------|
| P. | 11255·5 | P. | 16340·3 |
| „ | 8775·1 | „ | 11594·5 |
| | | | 16123·0 |
| | | | 11482·2 |

Na. The first seven doublets were allocated by RYDBERG, using the measurements by ÅNGSTROM, THALEN, and LIVEING and DEWAR. They were also so given by K. and R. The remainder were given by ZICKENDRAHT. The actual measures given in the list are by the observers indicated by the letters.

K. Both RYDBERG and KAYSER and RUNGE interchanged the S and D series, allocating those in the list to the S series. This was first corrected by RITZ.* The mistake is repeated in KAYSER'S 'Spectroscopie,' Bd. V. The line 6938·8 covers both KD₂ (3) and KS₁ (2). The pair at 4871 were first observed by L.D., but the more recent measurements by S. are inserted.

Rb. RL. refers to RANDALL, RE. to RAMAGE. The lines 3-6 were allocated by RYDBERG, and by K.R. The first doublet was observed and allocated by RANDALL. The second doublet has raised the question of whether Rb possesses satellites. The line 7757 has only been observed by SAUNDERS, who allocates it to RbD₁₁ (3), with 7759·5 as

* 'Ann. d. Phys.,' 12, 1903, p. 444.

satellite. But EDER and VALENTA observe 7759·5 and *not* 7757, whereas the former if a satellite should be fainter than the latter. The question is discussed in [I.] and also in the present communication, and the weight of evidence would appear to be against the existence of satellites in Rubidium. I have entered the third line as 6298·8 instead of K.R.'s value of 6298·7, because the former value agrees with independent observations by E.V., S., and E.H., and gives a better value for ν .

Cs. The first were observed and allocated by PASCHEN, the second first by LEHMANN, but the measures are those of PASCHEN. SAUNDERS was the first to draw attention to the satellites.

The last line, 5118, was observed by HARTLEY, and is clearly the $D_2(12)$ line. The corresponding $D_1(12)$ would be in the neighbourhood of 5256·96, or $D_2(9)$.

Mg, Ca. The lines were all assigned by RYDBERG. He also wrongly assigned two lines about 12000 to MgD(1). The measures are by K.R., except the ultra-red in Ca due to PASCHEN ('Ann. d. Phys.,' 29, p. 655).

Sr. Assigned and observed by K.R., except ultra-red due to PASCHEN.

Ba. Assigned by SAUNDERS ('Astrophys. Journ.,' 28, p. 223). The measures are those of K.R., except those with S. attached.

Zn. The lines down to $D_2(6)$ with the exception of the satellites were assigned by RYDBERG. The measures, as well as allocations of the others are by K.R.

Cd. Lines to $D_2(4)$, satellites excepted, assigned by RYDBERG. The remainder allocated and all the measures by K.R.

Eu. The Eu spectrum gives evidence of much collateral disturbance, and the unobserved D lines are possibly displaced in this way.

Hg. The D_{11} lines to $D_{11}(4)$ assigned by RYDBERG, to $D_3(5)$ satellite by K.R. $D_1(6)$ to $D_1(16)$ by MILNER ('Phil. Mag.,' (6), 20, p. 636).

Al. RYDBERG gives the first two doublets without the satellites and assigns 11280 wrongly to D(1). Further he assigns D lines to the S series, but the observations at his disposal were too inexact. The measures and allocations are by K.R.

In. RYDBERG down to $D_1(5)$ with satellites of first two. The remainder and all the measures by K.R. As in the S series it should be noted how the D_2 lines are more persistent than the D_1 .

Tl. RYDBERG gives all except from $D_1(10)$, and he gives D_2 down to $m = 15$. The measures given are by K.R. except those below 2105, which are due to CORNU.

The F Lines.

BERGMANN in 1908 ('Z. S. f. Wiss. Phot.,' 6, see also 'BEIBL.,' xxxii., p. 956) measured lines in the ultra-red spectra of the Alkalies and observed in Cs a number of doublets which clearly formed a series, and a few lines in Na, K, Rb which were evidently analogous. It was, however, RUNGE ('Astrophys. Journ.,' 27, p. 158; 'Phys. Z. S.,' 9, p. 1) who pointed out the dependence of the limit of the series on

D(2). The lines in the far ultra-red have since been observed by PASCHEN ('Ann. d. Phys.,' 33, 1910, p. 717). BERGMANN's lines began with the order $m = 4$, but in the lists above more recent and more accurate measures by others have been inserted. BN. refers to BERGMANN, RL. to RANDALL ('Ann. d. Phys.,' 33, p. 741), S. to SAUNDERS ('Astrophys. Journ.,' 20, p. 188).

In 1905 FOWLER ('Astrophys. Journ.,' 21, p. 84) discovered the lines in the F series for Sr, beginning with K.R.'s 4892, adding two sets of his own observations and also the two connected triplets given in the table. But he attempted to combine them all in one formula. The disarranged triplet for $m = 3$ is assigned in the text above from K.R. and LEHMANN ('Ann. d. Phys.,' 8, p. 647). In the same volume SAUNDERS ('Astrophys. Journ.,' 21, p. 195) added the last line and gave a similar series for Ca, commencing with 4586. The measures inserted in the table, however, are from later observations by BARNES (Bs.) ('Astrophys. Journ.,' 30, p. 14). SAUNDERS also suggested a corresponding series for Ba in which the separations are larger than those of the series assigned in the text. It is possible they may form a similar series connected with the enhanced series. The lines for RaF and allied sets are assigned also in the text above.

The F lines for Mg, Zn, Cd, Hg, Al, and Tl are all due to PASCHEN ('Ann. d. Phys.,' 29, p. 651, and 35, p. 860). In Hg, however, he assigns 17195 to a combination line, whereas in the text above it is assigned to F_1 .

[Notes, September 2, 1913.]

Note 1 — Since the present communication was read Messrs. FOWLER and REYNOLDS ('Roy Soc. Proc.,' 89, p. 137) have published more accurate and extended measurements of the series, and other lines of Mg. The limit of the D or S series appears to be somewhat higher than that adopted in the Table II. (p. 344), and the table will require the limit to be slightly raised to bring in multiples of Δ for the order differences. With FOWLER and REYNOLD's limit the mantissæ show rising values for the first few orders and then decreasing, an effect which has been explained in the text in similar cases by a collateral displacement in the limit after a particular order. If the limit be taken to be 39757.78 (*i.e.*, 6.7 higher than in the text), there results an order difference of $4\Delta_2$ between $m = 2$ and 3, and equal mantissæ afterwards down to $m = 9$, when there is a sudden change to a rising. If the limit is now raised by unity for these, the mantissæ can again be all equal. Now, a displacement of δ on the limit makes a change of 1.03, so that

the change can be explained by a collateral change of $(-\delta)D(\infty)$ for $m = 10-12$. The scheme is then as follows:—

| | | |
|--|----------|-------------------|
| | 2·828063 | (20) + 10 |
| | | $4\Delta_2$ |
| | 3·829715 | (79) - 36 |
| | 4·829715 | (190) + 9 |
| | 5·829715 | (362) + 58 |
| | 6·829715 | (626) - 580 |
| | 7·829715 | (945) - 173 |
| | 8·829715 | (2300) + 63 |
| | 9·829715 | (3200) + 1373 |
| Collaterals with $(-\delta)D(\infty)$ | { | 10·8297 (44) - 16 |
| | | 11·8297 (57) - 8 |
| | | 12·8297 (78) - 5 |
| | | 13·8297 (92) + 8 |

The arrangement is seen to be exceedingly simple. The value for $m = 1$ has been omitted as the evidence seems strong that Mg conforms to the Zn type and has no $D(1)$. If, however, it is retained, it is now $15\Delta_2$ below that for $m = 2$. The values of Δ_2 are so small that Mg can give no positive evidence for any arrangement. This is evidenced by the changed arrangements called for by more accurate values. The measures of FOWLER and REYNOLDS for the D lines are here adduced in order to complete Appendix II. :—

| | | |
|---------|---------|---------|
| 3097·03 | 3093·09 | 3091·19 |
| 2851·76 | 2848·54 | 2846·88 |
| 2736·63 | 2733·64 | 2732·16 |
| 2672·53 | 2669·66 | 2668·24 |
| 2632·98 | 2630·14 | 2628·73 |
| 2606·73 | 2603·98 | 2602·59 |
| 2588·37 | 2585·63 | 2584·32 |
| 2575·02 | 2575·30 | 2570·96 |
| 2565·00 | 2562·30 | 2560·96 |
| 2557·29 | 2554·70 | |
| 2551·22 | 2548·56 | |

Note 2, p. 357.—The effect of positive collaterals on $D(\infty)$ for $m = 5, 6, 7$ is to diminish the separations of the triplets, so that from $m = 5$ onwards they would show diminishing values. It is interesting to note that the observations bear this out.

Note 3, p. 380.—The F series of the alkalis. In K. the denominator 3·007542 has its mantissa 1·007542, and this is $14725(250 + ?)$ above that of K.F. (3), and $5\Delta = 14700$. This suggests that if K.F. (3) has a denominator $3 + d$, that of $F_{11}(2)$ is $2 + d$, and the 1182·9 (W.N.) is $F_{12}(2)$ with a satellite difference 2δ and 1346·3 is the collateral $F_{11}(2)(5\Delta)$. In Rb 3·001138 has its mantissa 13289(430 + ?) above that of RbF(3) and $\Delta = 12935$, so that should have a similar arrangement to that in K. and 2156 would correspond to $F_{11}(2)(\Delta)$.

Note 4, p. 383.—CaF(2). The line with wave number 16203·40 is possibly the F_{11} and F_{12} combined. If so, F_{12} is 16202·66 and is ·74 behind 16203·40, and the satellite might have displaced the observation towards itself from 16203·66. The actual separation would easily be 1·00 corresponding to a difference 2δ , a usual F satellite difference. 16024·72 would be 1·06 on the other side and would correspond to a collateral forming on the violet side.