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REPORT

ON

SERIES IN LINE SPECTRA.

BY

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PREFACE.

ALTHOUGH the spectra of elements and compounds were studied in the first instance chiefly as providing a powerful means of chemical analysis, it has long been recognised that a spectrum must contain an important clue to the structure and modes of vibration of the atoms or molecules which produce it Spectra, however, are most frequently very complex, and there could be but little hope of progress in the direction indicated if it were not possible to discover laws governing the distribution of the lines or bands of which they are composed The search for such laws has attracted many workers, and organised systems of lines which can be approximately represented by simple formulæ have been identified in the spectra of many elements and compounds The recognition of these regularities has naturally played a fundamental part in the development of theories of the origin of spectra and of the constitution of atoms and molecules The analysis of spectra has thus become one of the main objects of modern spectroscopy, stimulating the experimentalist to the extension of existing data, and providing material in a form suitable for the theoretical investigator

My purpose in the present report has been to give a comprehensive account of the development and present state of our knowledge of the regularities in spectra, as deduced from the spectra themselves, with but little regard to theories of their origin. The report is in two parts, the first of which gives a general account of spectral series, excluding those which occur in band spectra, while the second is intended to include the most authentic experimental data available in April, 1921 It is hoped that the tables of series lines, together with the references to lines which have not yet been classified, will suggest and facilitate further investigations The system of numeration of the series lines which has been adopted is that of Rydberg and Hicks, but if it should be found convenient to modify this numeration on theoretical grounds there should be no difficulty in making the desired alterations

The spectra dealt with are those obtained by optical methods, extending from the infra-red to the extreme ultra-violet The emissions of higher frequencies which have been revealed in the study of X-ray spectra do not form extended series of the kind met with in optical spectra, and have accordingly not been considered

I am indebted to Professor F A Saunders, of Harvard University, for much useful help during the preparation of the report, and especially for his kindness in supplying important observational material in advance of publication My thanks are also due to Col E H Grove-Hills, F R S , for the photograph reproduced in Fig 6, to Dr A S King, of the Mount Wilson Observatory, for Plate III *b*, and to Mr. N R Fowler for the negatives from which Plate IV was prepared. I also have pleasure in acknowledging the valuable assistance which has been rendered by Dr D Owen, Secretary of the Physical Society, and Mr H Dingle, B Sc , D I C , in reading the proof sheets

A FOWLER

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SOUTH KENSINGTON, LONDON.
February, 1922.

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PART I

GENERAL ACCOUNT OF SERIES.

CHAPTER I.

OBSERVATIONAL DATA

WAVE-LENGTHS AND WAVE-NUMBERS

The study of spectral series calls for a precise acquaintance with the nature of the available data, both as to the positions and characters of the lines involved

The position of a line in the spectrum is most generally indicated by the wave-length (λ) of the vibrations which produce it The unit of wave-length is the Ångstrom Unit, or "angstrom," as it is now beginning to be called It was intended to equal 10^{-10} metre, and is accordingly often called the "tenth-metre." It is also equivalent to 10^{-8} cm , or 0 0001μ, where μ is the micron, or thousandth of a millimetre Wave-lengths in the visible spectrum range from about 3,900A to 7,600A (A being the modern abbreviation for the angstrom) For the long waves in the infra-red, however, μ is often taken as the unit, so that λ12,500A, for example, would be indicated by 1 25μ

The wave-length scale was introduced by Ångstrom in 1869, and until about the year 1900, wave-lengths were referred to his determinations as standards , they were meant to represent the wave-lengths in air at 16°C and 760mm pressure Later work, however, proved that Ångstrom's values were about 1A too low, and, about 1896, the scale was superseded by that of Rowland, which referred to wave-lengths in air at 20°C and 760mm Still more recently it has been found that Rowland's scale was based upon erroneous values for the *D* lines of sodium, besides being affected by other small errors, and Rowland's scale is now being gradually replaced by the "International" scale The latter is founded upon interferometer determinations of the wave-length of the red line of cadmium, which is much superior to the sodium lines in point of sharpness The wave-length adopted for this line by the International Solar Union* is 6438 4696, being the value determined by Benoit, Fabry, and Perot, and in close accordance with a previous measurement by Michelson The precision of this value for the standard line is such that the unit of wave-length which it defines can differ but little from 10^{-10}m , but to avoid all misunderstanding the unit of wave-length defined by the cadmium line has been called the International Angstrom , and is indicated in tables by the letters "*I A*" , we thus have

$$I\,A = \frac{\text{Wave-length of red Cd line in dry air at 15°C , 760 mm , with } g=980\ 67}{6438\ 4696}$$

The majority of published wave-lengths, however, have been expressed on Rowland's scale, and if new determinations have not become available, it is necessary to reduce the Rowland values to the international scale in any precise work on series From a comparison of the two scales, Kayser† has derived the corrections which are shown in Table I These corrections include the small differences depending upon the differences in the standard temperatures of the two scales (20°C for Rowland, and 15°C for the international scale)

In connection with spectral series it becomes important to specify the positions

* Trans Int Sol Union, **2**, 20, 28 (1907) (The Solar Union is now absorbed into the International Astronomical Union)

† Handbuch der Spectroscopie, **6**, 891 (1912)

of lines either in "oscillation-frequencies," or by "wave-numbers" The most fundamental figures are the oscillation-frequencies, since these are not changed when the medium is changed But the determination of frequency requires an exact knowledge of the velocity of light, and it is more convenient to use the wave-number, or number of waves per centimetre, thus—

$$\text{Wave-number} = \nu = \frac{10^8}{\lambda \text{ in angstroms}}$$

Correction to Vacuum

Wave-numbers as well as wave-lengths vary with the medium in which the vibrations are propagated, and it is therefore necessary to reduce them to standard conditions They are accordingly reduced to their values *in vacuo*, and when thus corrected the wave-numbers are strictly proportional to the oscillation-frequencies This correction can be made when the refraction and dispersion of air have been determined with sufficient accuracy Thus—

$$\lambda_{vac} = \mu \lambda_{air}, \text{ or } \Delta\lambda = \lambda_{vac} - \lambda_{air} = \lambda_{air}(\mu - 1)$$

where μ=the refractive index of air

The refractive index, of course, varies with the density, and therefore with the temperature and pressure, of the air Kayser and Runge have given a formula indicating the value of μ for air at 760mm pressure, and temperature 0°C, and have derived a table of corrections to vacuum applicable to wave-lengths determined in air at 20°C and 760mm pressure * The most recent observations have been made at the Washington Bureau of Standards by Meggers and Peters,† who give the following formulæ for the refractive indices of dry air at 760mm pressure, and temperatures 0°C, 15°C and 30°C, λ being expressed in angstroms —

$$0°C \quad (\mu-1)_0 \times 10^7 = 2875\ 66 + \frac{13\ 412}{\lambda^2 \times 10^{-8}} + \frac{0\ 3777}{\lambda^4 \times 10^{-16}}$$

$$15°C \quad (\mu-1)_{15} \times 10^7 = 2726\ 43 + \frac{12\ 288}{\lambda^2 \times 10^{-8}} + \frac{0\ 3555}{\lambda^4 \times 10^{-16}}$$

$$30°C \quad (\mu-1)_{30} \times 10^7 = 2589\ 72 + \frac{12\ 259}{\lambda^2 \times 10^{-8}} + \frac{0\ 2576}{\lambda^4 \times 10^{-16}}$$

These observations have been utilised in the construction of a table showing the corrections which must be applied to wave-lengths and wave-numbers measured in air to convert them to their values in vacuum An extract from the Washington tables is given in Table II., indicating the amounts to be added to wave-lengths in dry air at 15°C and 760mm, and therefore directly applicable to wave-lengths on the international scale ‡ The conversion to wave-numbers can readily be effected by the use of a table of reciprocals with seven-place arguments

When the wave lengths are expressed on Rowland's scale, which refers to 20°C, the simplest procedure is to reduce them to the international system by means of

* Handbuch, 2, 514

† Scientific Papers of the Bureau of Standards, Washington, No 327 (1918)

‡ Some of the figures have been slightly amended in Astrophys Jour, 50, 56 (1919)

Table I, and then to correct them to vacuum by adding the corrections given in Table II

The corrections of infra-red wave-lengths to the international system and to vacuum are subject to some uncertainty For wave-lengths greater than 10,000A, however, the correction to the international scale has but little influence on the wave-numbers Thus, at λ10,000 the correction increases the wave-number by 0·4, at λ20,000 by 0 2, and at λ40,000 by 0 1. Corrections to vacuum may be determined approximately by extrapolation of the Washington formula for the refractive index of air (*See* Table II*a*)

Arc and Spark Spectra Enhanced Lines

The investigation of spectral series often requires a knowledge of the behaviour of the lines when produced under different conditions of excitation The spectra of metallic elements are most frequently obtained by the use of the electric arc or by the condensed discharge from an induction coil, and the spectrum is usually different in the two cases (*See* Plate IV) On passing from the arc to the spark it often happens that some of the lines are diminished in relative intensity, while others become brighter, and new lines frequently make their appearance in the spark Lines which are relatively enhanced in brightness on passing from the arc to the spark, or which only occur in the spark spectrum, were called *Enhanced Lines* by Lockyer, and this name has been generally adopted Lines which appear in the arc and tend to diminish in intensity in the spark are then distinguished as *Arc Lines* The term "arc lines," it will be seen, does not necessarily include *all* the lines which appear in the arc spectrum, and, similarly, the spark spectrum most frequently includes some surviving arc lines as well as enhanced lines

It is convenient to distinguish at least three classes of enhanced lines (I) Enhanced lines like the *H* and *K* lines of calcium, which are quite strong in the arc (and appear with greater intensity in the spark), (II) Lines which only appear with feeble or moderate intensity in the ordinary arc, such as the enhanced lines of iron and titanium, (III) Lines which do not appear in the ordinary arc, but are strongly developed under spark conditions, as in the case of the well-known magnesium line λ4,481 It would thus seem that while the energy of the arc is in some cases sufficient to develop the enhanced lines, the greater energy of the disruptive spark is required to give rise to them in the case of some of the elements In other words, different elements respond differently to a given stimulus

It should be mentioned that enhanced lines are also often found to appear in a region close to the poles of a metallic arc, and when the arc is passed in an atmosphere of hydrogen, or in a vacuum,* they frequently become very pronounced

Similar variations of the line spectrum are also observed in the case of many gases, including helium, oxygen, and nitrogen, when the electric discharges which excite them are varied in intensity From analogy with metallic spectra, certain lines which thus appear in the spectra of gases under the action of powerful discharges may quite properly be classed as enhanced lines In some cases, a succession of spectra appear as the intensity of the discharge is gradually increased Oxygen, for example, gives a spectrum corresponding to the arc spectrum when the discharge is feeble, new lines appear with a moderate increase in the intensity, and still others when the strongest discharges are passed through the gas; the three

* Fowler and Payn, Proc Roy Soc, **72**, 253 (1903)

different classes of lines are then conveniently distinguished as arc, spark and "super-spark," or as *O*I., *O*II , and *O*III * Silicon shows four such stages

As might be expected, arc lines and enhanced lines have not been found to be associated in the same family of series

Intensities and Characters of Lines

In the investigation of series spectra, it is important also to take into account the intensities and physical characteristics of the lines involved A convenient standard scale of intensities has not yet been introduced into spectroscopic tables, and tabulated intensities are, for the most part, merely rough estimates on an arbitrary scale, in which 10 represents the strongest and 1 the weakest lines This range, however, is often too restricted, and in some tables, notably those of Exner and Haschek, the very strongest lines are represented by the higher numbers 15, 20, 30, 50, 100, 200, 500 and 1,000 In order to extend the scale in the opposite direction, some observers also follow Rowland's convenient plan of indicating very faint lines by 0, 00, 000, and 0000, the latter being at the limit of visibility A method of estimating intensities on an absolute scale has been devised by Nicholson and Merton,† but its use has so far been restricted to the spectrum of helium

While some lines are sharp and well-defined, others may be shaded on one or both edges, and others again, especially in arc spectra, may be reversed These different appearances are usually indicated in spectroscopic tables by the addition of letters to the numbers showing the intensities There is, unfortunately, a considerable diversity in the notations adopted by different observers, and it is usually necessary to rely upon an author to describe the symbols employed in any particular case Some of the principal systems which have been adopted are as follows —

Character	Watts	Kayser.	Exner and Haschek.	This Report.
Sharp	*s*	*s**	—	*s*
Nebulous or diffuse	*n*	*u*†	+	*n*
Broad	*b*	*u*†	*br*‡	*b*
Broad, but sharp on red edge	b^r	—	—	—
Diffuse towards violet	—	*v*, or *uv*	*v*	*v*
Broad, but sharp on violet edge	b^v	—	—	—
Diffuse towards red	—	*r*, or *ur*	*r*	*r*
Reversed	*r*	*R*	*u*§	*R*
Double	—	*d*	*d*	*d*

* Scharf † Unscharf ‡ Breit § Umgekehrt

The symbols in the last column will be adopted in this report, and it is to be understood that the absence of any symbol indicates that the line is of ordinary sharpness, but not specially sharp

In a reversed line there is a broad bright line, diffuse at the edges, which is produced by the denser vapour at the core of the arc or spark used as the source of light, and a narrow absorption line superposed upon this which originates in the cooler and less dense vapour in the outer envelope The reversal is sometimes unsymmetrical

* Fowler and Brooksbank, Monthly Notices, R A S , **77**, 511 (1917)
† Phil Trans A, **217**, 242

It should be noted that lines which are ordinarily diffuse in an arc spectrum can usually be obtained as sharp lines by passing the arc in a vacuum There are, in fact, examples of series which might never have been recognised as such if reliance had been placed upon observations of the arc or spark in air, as the more refrangible members are sometimes diffused to the degree of invisibility.

Lines which belong to the same series are usually similar in character, but an apparent exception has been noted by Royds in barium ,* in this case the lines of a triplet in the yellow appear to be widened unsymmetrically towards the red, while the more refrangible triplets are shaded towards the violet The corresponding triplets of calcium present a less extreme exception, the blue triplet being sharply defined, while succeed ng members are diffuse towards the violet, the associated infra-red triplet may possibly be shaded towards the red

The Schumann and Infra-Red Regions

The ordinary instruments which are employed in spectroscopic work do not permit the investigation of the whole range of the spectrum Spectroscopes with prisms and lenses of glass only serve for a small part of the ultra-violet, and a small part of the infra-red, in addition to the visible spectrum When quartz is substituted for glass the range may be extended to about λ 1,850 in the ultra-violet, but for shorter wave-lengths special arrangements become necessary This part of the spectrum was first investigated by Schumann, and is commonly called the Schumann region In the first instance, fluorite was substituted for quartz, and on account of the opacity of air for the short waves the whole apparatus, including the photographic plate, was placed in an exhausted air-tight case The ordinary gelatine plates being strongly absorbent for short waves, special " Schumann plates " with a very thin coating of gelatine are also necessary Concave gratings have been successfully employed by Lyman and others, and have permitted observations beyond the region for which fluorite is transparent Details of the instruments and methods of work have been given by Lyman in his book on " The Spectroscopy of the Extreme Ultra-Violet "†

Observations have now been extended as far as λ 584A by McLennan‡ and to 220A by Millikan § Wave-lengths in this region are usually tabulated as observed, and no correction to vacuum is required in the calculation of wave-numbers It should be noted that since $d\nu = -10^8/\lambda^2\, d\lambda$, errors in the wave-length are greatly multiplied in the conversion to wave-numbers in this region as compared with the less refrangible parts of the spectrum

At the red end of the spectrum, direct photographs on plates stained with dicyanin have been obtained by Meggers as far as λ10,000A || The further infra-red is investigated by thermo-electric methods, employing spectroscopes having optical parts of rock-salt or making use of gratings Extensive work with special reference to series lines has been carried on in this region by Paschen¶ and by Randall **

The extension of observations into the extreme ultra-violet and infra-red has been of great value in the elucidation of the structure of spectral series, as will appear in due course

* Astrophys Jour , **41**, 154 (1914)
† Longmans (1914)
‡ McLennan, Proc Roy Soc , A , **95**, 2-8 (1919)
§ Astrophys Jour , **52**, 47 (1920)
|| Scientific Papers of the Bureau of Standards, Washington Numbers 312, 324, 345, &c
¶ Ann d Phys , (4) **27**, **29**, **33** (1908-10), and other Papers
** Astrophys Jour , **34**, 1 (1911) , **42**, 195 (1915) , **49**, 42, 54 (1919)

SOURCES OF DATA

The following references to the principal collected tables of wave-lengths and photographs of spectra may be usefully appended to this chapter

(1) W MARSHALL WATTS "Index of Spectra," with numerous appendices. (Heywood, Manchester.)

(2) F. EXNER and E HASCHEK "Wellenlangen Tabellen fur Spectralanalytische Untersuchungen auf Grund der Ultra-Violetten Funkenspektren der Elemente" (Leipzig and Wien, 1902)

(3) F. EXNER and E HASCHEK "Wellenlangen Tabellen . . . Bogenspektren" (1904)

(4) F EXNER and E HASCHEK "Die Spektren der Elemente bei Normalen Druck" I, Hauptlinien der Elemente und Codex der Starken Linien im Bogen und Funken II, Die Bogenspektren (Leipzig and Wien, 1911.)

(5) A HAGENBACH and H KONEN "Atlas der Emission Spectra" (Jena, 1905) English edition by A S King (W Wesley & Son, London)

(6) J M EDER and E VALENTA "Atlas Typischer Spektren" (Wien, 1911)

(7) H KAYSER "Handbuch der Spectroscopie," Vols V and VI. (Leipzig, 1910, 1912) (These include practically all the measures to the dates of publication)

Many valuable series of measures have since been published in the "Astrophysical Journal" and in the "Zeitschrift fur Wissenschaftliche Photographie" The "International Tables of Constants" also include collections of spectroscopic measurements. Collections of tables for the Schumann region are given in Lyman's book

CHAPTER II.

HISTORICAL NOTE

1869—1879

The earlier attempts to discover laws governing the distribution of lines in spectra were controlled mainly by the supposition that the vibrations which give rise to the lines might be similar to those which occur in the phenomena of sound, and might correspond with harmonical overtones of a single fundamental vibration. In that case the ratios of the wave-lengths of different lines would be expected to be represented by comparatively small integral numbers Lecoq de Boisbaudran* believed that he had discovered such relations among the bands of nitrogen, but more exact measurements which were made later failed to verify his conclusions In 1871, however, it was pointed out by Dr. Johnstone Stoney† that the wave-lengths of the first, second, and fourth lines of hydrogen were in the inverse ratio of the numbers 20, 27, and 32, and the accuracy of these ratios strongly suggested the existence of genuine harmonical relations

The admirable experimental work of Liveing and Dewar,‡ which extended well into the ultra-violet part of the spectrum, provided valuable data for further investigations, and several important features of associated lines were revealed by these observations In the spectrum of sodium it was observed that successive pairs of lines were alternately sharp and diffuse, and that the pairs generally became fainter and more diffuse as they were more refrangible, at the same time the distance between successive pairs was diminished (Compare Plate I) It was remarked that the whole series, excluding the "D" pair, looked very like repetitions of the same set of vibrations in a harmonic progression,§ and it seemed that harmonic relations could be found to subsist between some of the groups The whole series, however, could not be represented as simple harmonics of one set of six vibrations with any degree of probability Somewhat similar results were also obtained for potassium, and, later, for the triplets of magnesium ‖

The Spectrum of Hydrogen

The discovery by Huggins¶ of a number of prominent lines in the ultra-violet spectra of Sirius and other white stars (Fig 1), which seemed to be a continuation of the regular series of hydrogen lines in the visible spectrum, led to further search for harmonic ratios in this spectrum on the part of Dr. Johnstone Stoney.** Evidence that the lines in question were all members of the same physical system was found in the fact that when their positions were plotted as abscissæ against ordinates which increased uniformly, they fell upon, or very near, a definite

* Comptes Rendus, **69**, 694 (1869)

† Phil Mag, **41**, 291 (1871)

‡ Proc Roy Soc, **29**, 398 (1879), Collected Papers on Spectroscopy, p 66

§ Liveing and Dewar were careful to explain that their reference to harmonic series of lines did not imply that the lines were thought to follow the arithmetical law of an ordinary harmonic progression, but to be comparable with the overtones of a bar or bell

‖ Proc Roy Soc, **32**, 189 (1881)

¶ Phil Trans, **171**, Pt II, 669 (1880)

** Quoted by Huggins

curve A new departure in the investigation was the substitution of the scale of " wave-frequencies " (the reciprocals of the wave-lengths) for that of wave-lengths On forming the first and second differences of these wave-numbers, Dr Stoney concluded (erroneously) that the irregularities in the second differences were too great

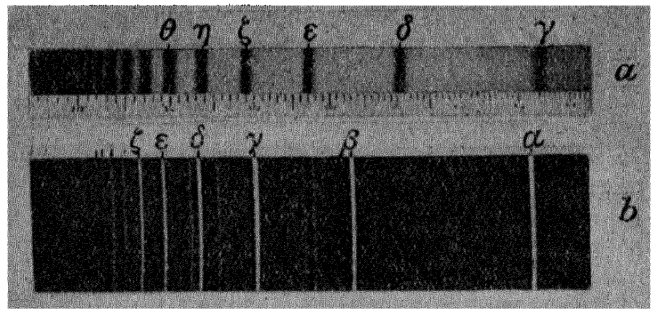


FIG 1 —THE SPECTRUM OF HYDROGEN (*a*) IN SIRIUS, (*b*) IN VACUUM TUBE

to be attributed to errors of measurement, and that the lines did not fall exactly on a smooth curve Hence it was thought that the lines were not consecutive members of a single series, but members of two or more series, and attention was drawn to several apparently harmonic relations between selected groups of lines

SCHUSTER'S CONCLUSIONS

A discussion of the evidence for the existence of harmonic ratios in spectra was given by Schuster in 1881,* and although it was concluded that the number of such ratios was not greater than might be attributed to chance, Schuster clearly recognised that there might be some undiscovered law, which, in special cases, resolved itself into the law of harmonic ratios In the light of our present knowledge this is evidently the case for the ratios of the hydrogen lines discovered by Stoney, which follow naturally from the simple law which connects *all* the lines of the series in question, the ratios thus have no special significance, but it is interesting to note that they contain the germ of the true law, and might well have led to its discovery

That some law existed was sufficiently evident from the distribution of the lines in the hydrogen spectrum, and from the maps of the spectra of sodium and potassium which had been given by Liveing and Dewar, but progress was greatly retarded by the lack of sufficiently exact measurements of the wave-lengths of the lines Schuster found, for instance, that although all the lines of sodium appeared to be double, and many of those of magnesium triple (compare Plate II), the measurements then available showed no regularity in the distances separating the components Nevertheless, the fact that the hydrogen lines approach each other rapidly as they pass towards the ultra-violet, and that characteristic groups which are repeated several times in other spectra also come nearer and nearer together in the more refrangible parts of the spectrum, was considered by Schuster to furnish a safer basis for further research than the hypothesis of harmonic ratios It was, in fact, in this direction that subsequent advances were made

* Proc Roy Soc , **31**, 337 (1881) , Brit Assoc Report (1882), p 120

Law of Constant Separations.

A fact of great importance was established by Hartley in 1883,* namely, that the components of doublets or triplets occurring in the same spectrum are of identical separation provided that the positions of the lines are expressed on the scale of oscillation frequencies (or of reciprocal wave-lengths, which are proportional to the frequencies) By the discovery of this law of constant separations, pairs or triplets occurring in different parts of the same spectrum could be associated with certainty.

A further valuable contribution on the experimental side was made by Liveing and Dewar in 1883,† when they gave an account of their work on the ultra-violet spectra of the alkali and alkaline earth metals, and of zinc, thallium, and aluminium, in each of which there are well-marked series The characteristics which they had previously noted in the case of sodium and magnesium were then found to be equally pronounced in other spectra, and several new series were recorded, including what are now called the principal series of lithium, sodium, and potassium These observers, however, did not investigate the laws of the series which they described with such completeness and accuracy

Balmer's Law for Hydrogen

A new era commenced in 1885, when the law of the hydrogen series was discovered by Balmer ‡ The number of lines then known to belong to this series, as produced in the laboratory, had been increased to nine by W H Vogel,§ and five more had been recorded by Huggins in the spectra of the white stars Balmer found that the series could be represented, probably within the limits of error of the observations, by a formula of the type

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

where h is a constant for the series, and m and n are whole numbers For the actual lines, using Ångstrom's measures of the first four lines, he gave the formula

$$\lambda = 3645\ 6\frac{m^2}{m^2-4}$$

where m takes the values, 3, 4, 5, ...

Thus

	Calcd λ	Obsd λ	$O-C$
$H_\alpha = \frac{9}{5}h$	=6562 08	6562 10	+0 02
$H_\beta = \frac{4}{3}h$	=4860 80	4860 74	−0 06
$H_\gamma = \frac{25}{21}h$	=4340 00	4340 10	+0 10
$H_\delta = \frac{9}{8}h$	=4101 30	4101 20	−0 10

* Jour Chem Soc , **43**, 390 (1883)
† Phil Trans , **174**, 187 (1883) , Collected Papers, p 193.
‡ Wied Ann , **25**, 80 (1885)
§ Monatsb Königl Acad , Berlin, July 10 (1879)

The extrapolation to the ultra-violet lines gave values roughly corresponding to the measured wave-lengths, but it remained rather doubtful whether the law was exact or only an approximation to the true formula for the entire series. Subsequent investigations, however, have shown that the law, with a slightly amended constant, represents the whole series with extraordinary accuracy.

Although the hydrogen spectrum is in a sense typical of all series, the simple Balmer formula with modified values of h is not applicable to series in general Nearly all attempts to represent series of lines by formulæ, however, have been based upon the Balmer law, with the introduction of one or more correcting terms

Balmer's discovery of the law of the hydrogen series, together with Hartley's law of constant separations and Liveing and Dewar's experimental data, provided a sound basis for further research

First Results of Kayser and Runge

Shortly after the discovery of Balmer's law, the investigation of series spectra was taken up by Kayser and Runge, and by Rydberg The first results of the former were published in 1888 by Runge,* who announced that formulæ had been found for series of lines of elements other than hydrogen Their equations were of the form

$$\lambda = \frac{1}{a+bm^{-1}+cm^{-2}} \quad \text{or} \quad \lambda = \frac{1}{a+bm^{-2}+cm^{-4}}$$

where a, b, c are constants special to each series, and m assumes consecutive values of the series of whole numbers, beginning with 3 The following formula was given for the principal series of lithium, m being 3 for the line $\lambda 3232$ –

$$\lambda \text{ (in mm)} = \frac{1}{4341{\cdot}4+136\,5m^{-1}-11635m^{-2}}$$

It will be observed that the formula is a more general form of that given by Balmer for hydrogen, which may be written

$$\lambda = \frac{hm^2}{m^2-4} = \frac{1}{\frac{1}{h}-\frac{4}{hm^2}} = \frac{1}{a-bm^{-2}}$$

Kayser and Runge were quick to recognise the need for a more accurate knowledge of wave-lengths in such inquiries, and courageously embarked on a new series of determinations with the aid of a large concave grating, beginning with the spectrum of iron as a convenient standard of comparison for purposes of interpolation †

The Work of Rydberg

Rydberg made use of data already to hand, and his investigations are of the utmost importance as having laid the foundation for all subsequent attempts to show the connection between different series occurring in the same spectrum His first

* Brit Assoc Report (1888), p 576

† Abhandl der Berlin Akad (1890)

memoir was presented to the Swedish Academy of Sciences towards the end of 1889* and gives a comprehensive account of the results at which he had then arrived. As in the case of Kayser and Runge, the ultimate purpose of his inquiries was to gain a more intimate knowledge of the structure of atoms and molecules, and notwithstanding the imperfect data then at his disposal, he discovered most of the important properties of series, and foreshadowed discoveries which were made later, when experimental work provided the necessary data

Rydberg commenced his work by sorting out doublets and triplets, largely from the tables given by Liveing and Dewar and by Hartley, and in this way ascertained the lines which might properly be associated in the same set of formulæ Although the terms "doublet" and "triplet" had in general been understood to signify groups of lines not very far apart, Rydberg showed that there were true doublets and triplets in which the components were remote from each other, so that while one component might be in the visible spectrum, another might even be situated in the ultra-violet, other lines occupying the intermediate spaces Hartley's law of constant separations was thus confirmed and extended, with the proviso that the law was applicable only to members of series of the same species

Like Johnstone Stoney and Hartley, Rydberg employed the reciprocals of the wave-lengths in place of the oscillation frequencies themselves, but gave them a more definite meaning by defining the "wave-number" as the number of wave-lengths per centimetre, that is, $10^8/\lambda$ in Ångstrom Units He pointed out that the use of wave-numbers not only saves a great deal of calculation, but is important in theoretical considerations

The observation by Liveing and Dewar that pairs or triplets are alternately sharp and diffuse enabled Rydberg to distinguish two species of series, in addition to a third species comprising the ultra-violet lines which the same observers had photographed in the spectra of Li, Na, and K The first terms of the latter species, which are the most intense in the spectra, are situated in the visible spectrum and had not previously been associated with the ultra-violet series Three chief species of series were thus recognised as being superposed in the same spectrum, namely —

Principal, including the strongest lines
Diffuse, of intermediate intensity
Sharp, including the weakest lines,

and the members of each series might be single, double, or triple

In each series the distance from line to line diminishes rapidly on passing to the more refrangible parts of the spectrum, the lines thus converging towards a definite limit, and in a normal series, intensities also diminish in regular order In a graphical representation with the observed wave-lengths (λ) or wave-numbers (ν)† of a series as abscissæ, and consecutive whole numbers (m) as ordinates, Rydberg found that each series was represented by a regular curve, which appeared to be similar in shape for all series, and to approximate to a rectangular hyperbola (*see*

* Kongl Svenska Vet-Akad Handlingar, Bandet 23, No 11 (1890) [in French] Abstracts were given in Comptes Rendus, Feb (1890), Zeitschr Phys Chem, February (1890), and Phil Mag, April (1890)

† Rydberg represented wave-number by n, but analogy with the λ always employed for wave-length suggests that ν, as used by Ritz, is more appropriate

Figs 2 and 3, pp 14 and 17) A rough representation of several series was in fact obtained by the use of the hyperbolic formula :—

$$\nu = \nu_\infty - \frac{C}{m+\mu}$$

where ν is the wave-number of a line, m its order number, and ν_∞, C, and μ are constants special to each series, ν_∞ is the *limit* of the series, being the value of ν when m is infinite.

Further investigation, however, led to the conclusion that the wave-number should be represented by the equation

$$\nu = \nu_\infty - f(m+\mu)$$

where the form of the function, and any additional constants, would be the same for all series The simple hyperbolic formula did not fulfil this imposed condition, as the value of C was found to vary very considerably from one series to another. Rydberg then proceeded to investigate the next simplest form of the function, and adopted it in his subsequent work, namely,

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

where N is constant for all series

When μ is zero this formula becomes identical with that of Balmer for hydrogen, which in terms of wave-numbers, may be written

$$\nu = \nu_\infty \frac{m^2-4}{m^2} = \nu_\infty - \frac{4\nu_\infty}{m^2} = \nu_\infty - \frac{N}{m^2}$$

The constant N could thus be calculated from the hydrogen lines, which gave the value 109,721 6 This, however, was deduced from wave-lengths in air, expressed on the scale of Ångstrom, and was recalculated later as 109,675 00 from wave-lengths on Rowland's scale, corrected to vacuum * This number appears in the formulæ for other series, and is generally designated the " Rydberg Constant " Its value on the international scale has recently been given by W E Curtis as 109,678 3

Rydberg fully recognised that the formula which he employed was only an approximation to the true function of m or of $(m+\mu)$, but by its aid he was able to trace a large number of series in the spectra of different elements, and to deduce most of the important properties of series in general

Kayser and Runge's Formula

Almost immediately after the announcement of Rydberg's results, Kayser and Runge published an account of their investigations of the spectra of the alkali metals † These observers also adopted the scale of wave-numbers per centimetre, and employed the formula

$$\nu = A - \frac{B}{m^2} - \frac{C}{m^4}$$

where ν is the wave-number, m the order number of a line, and A, B, C three

* Congrès Internat de Physique, Paris (1900), p 211.
† Abhandl. der Berlin Akad (June 5, 1890)

constants special to each series; A is evidently the limit of the series, B is of the same order of magnitude as Rydberg's constant N, but C varies widely from one series to another The formula was by no means capable of giving an accurate representation of all the lines of a series, and is inferior to that of Rydberg inasmuch as it fails to show the important connection between the Principal and Sharp series A large number of series and many of the properties of series already described by Rydberg, however, were independently discovered by its use

Kayser and Runge's formula has passed its period of usefulness, and practically all the newer formulæ represent attempts to improve the original equation of Rydberg Kayser and Runge, however, made important contributions to the subject by their improved tables of the spectra of many elements,* and by their determinations of the refractive indices of air† which permitted the correction of the wave-numbers to vacuum.

* Abhandl. der Berlin Akad (1891, 1892, 1893)
† Abhandl. der Berlin Akad (1893)

CHAPTER III.

CHARACTERISTICS OF SERIES.

General Formula for Hydrogen.

It should be clearly understood that the series spectrum of hydrogen is of exceptional simplicity. The Balmer series, however, does not constitute the whole of the hydrogen spectrum Another series in the infra-red was predicted by Ritz, and two members at $\lambda 18{,}751$ and $\lambda 12{,}817$ 6 have been observed by Paschen. There is also a series in the Schumann region, of which three members have been photographed by Lyman. All the series are included in the general formula

$$\nu = N\left(\frac{1}{m_1^2} - \frac{1}{m^2}\right), \quad m_1 < m$$

where $m_1 = 1$ for Lyman's series, $=2$ for the Balmer series, and $=3$ for the Ritz-Paschen series. For wave-numbers on the international scale, corrected to vacuum, $N = 109{,}678$ 3 (Curtis).

A graphical representation of these series is given in Fig 2

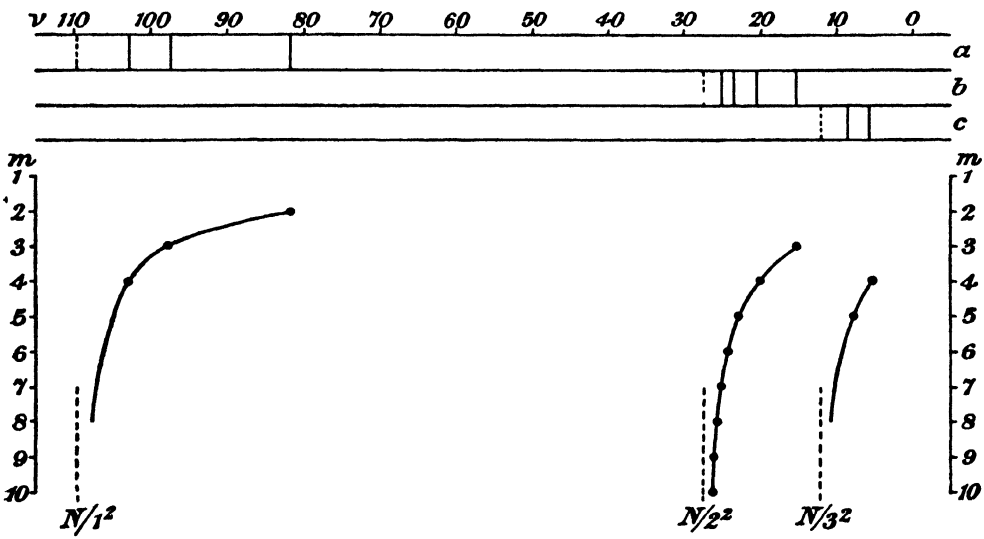


Fig 2.—The Three Series of Hydrogen

(*a*) = Lyman series, (*b*) = Balmer series, (*c*) = Ritz-Paschen series

The Four Chief Series of Other Elements

The work of Rydberg, and that of Kayser and Runge, revealed the existence of a large number of series, each of which is generally similar to the Balmer series of hydrogen In each series the lines become closer, with diminishing intensities in passing from the red towards the violet end of the spectrum, and converge to a

definite limit (Fig 3, p. 17) Theoretically, the number of lines in a series is infinite, but no series have actually been traced to their limits. There are no known series in which the lines converge towards the less-refrangible part of the spectrum.

In the general case there are several series superposed in the same spectrum. Several such series are intimately related to each other and may be conveniently regarded as forming a " system " of series. Four of the related series have a certain amount of independence and may be considered to be the chief series of a system. The remainder may be looked upon as derived series.

Three of the chief series were recognised by Rydberg and by Kayser and Runge, namely, in order of intensity —

Principal, Diffuse, Sharp (Rydberg).
Principal, first Subordinate, second Subordinate (Kayser and Runge).

Rydberg's names are most commonly used and are conveniently abbreviated to P, D, S, while the respective limits may be represented by $P\infty$, $D\infty$, $S\infty$

The fourth chief series long escaped detection because many of them occur in the infra-red, in which region they were first observed by Bergmann.* They are called " Bergmann series " by some writers, but as they do not all occur in the infra-red, and were not all discovered by Bergmann, the name is not specially appropriate From theoretical considerations Hicks has named them the " Fundamental " or " F " series, and though they are probably not more fundamental than the other chief series, the name has been so much employed that it will be convenient to retain it for the purposes of the present report

Although less exact than some of the amended forms which have since been proposed, Rydberg's formula is usually a sufficient approximation to bring out the main characteristics of a system of series, and its simplicity is a great advantage in approaching the subject This formula will accordingly be adopted for descriptive purposes, namely —

$$\nu_m = A - \frac{N}{(m+\mu)^2}$$

where A is the limit of the series, N the Rydberg constant for hydrogen, and the wave-numbers ν_m are obtained by assigning successive integral values to m, μ may be regarded as a decimal part to m, though it is sometimes greater than unity Each series is thus represented by a limit, and a series of " variable parts " or " terms " forming a " sequence "

The four chief series may be represented by the Rydberg formulæ —

Principal	$P(m) = P\infty - N/(m+P)^2$	$m=1, 2, 3 \ldots$
Sharp	$S(m) = S\infty - N/(m+S)^2$	$m=2, 3, 4 \ldots$
Diffuse	$D(m) = D\infty - N/(m+D)^2$	$m=2, 3, 4 \ldots$
Fundamental	$F(m) = F\infty - N/(m+F)^2$	$m=3, 4, 5 \ldots$

where $P(m)$, for example, means the m-th line of the P series, and P, S, D, F indicate the values of μ in the respective series

These formulæ represent the four chief series of a " singlet " system, but in many systems each member of a series is a doublet or a triplet

* Dissertation, Jena (1907), Zeit Wiss Phot, 6, 113, 145 (1908)

Relations Between the Chief Series

The relations between the P, S, and D series were most completely traced by Rydberg His method may be usefully illustrated by reference to the spectrum of lithium, which consists of doublets close enough to be regarded as single lines Rydberg's original formulæ, which are sufficiently accurate for our purpose, were as follows :—

$$P(m) = 43{,}487\ 7 - \frac{109{,}721\ 6}{(m+0\ 9596)}$$

$$S(m) = 28{,}601\ 1 - \frac{109{,}721\ 6}{(m+0\ 5951)^2}$$

$$D(m) = 28{,}598\ 5 - \frac{109{,}721\ 6}{(m+0\ 9974)^2}$$

These formulæ, and similar ones calculated for series of other elements, showed, in the first place, that the limits of the S and D series were probably identical, *i e*, $S\infty = D\infty$.

Next, it was found that $m=1$ in the variable part of the formula for $S(m)$ gave approximately the limit of the P series, thus

$$N/(1\ 5951)^2 = 43{,}123\ 7$$

And, similarly, $m=1$ in the formula for $P(m)$ gave approximately the limit of the S series, thus

$$N/(1\ 9596)^2 = 28{,}573\ 1$$

From such considerations Rydberg concluded that $P\infty = N/(1+S)^2$ and $S\infty = D\infty = N/(1+P)^2$, so that the three series could be represented by

$$P(m) = \frac{N}{(1+S)^2} - \frac{N}{(m+P)^2}$$

$$S(m) = \frac{N}{(1+P)^2} - \frac{N}{(m+S)^2}$$

$$D(m) = \frac{N}{(1+P)^2} - \frac{N}{(m+D)^2}$$

The Rydberg-Schuster Law

The first line of the P series (given by $m=1$) is thus identical with that given by $m=1$ in the S formula, but with opposite sign *i e*, $S(1) = -P(1)$ It follows that *the difference between the limit of the P series and the common limit of the D and S series is equal to the wave-number of the first line of the P series* This important rule was clearly included in the formulæ given above, but Rydberg did not express it in these terms until 1896,* in which year Schuster† also independently announced its discovery, apparently by reference to the limits of the numerous series which had been calculated by Kayser and Runge The law of limits is thus generally known as the Rydberg-Schuster law, and is expressed symbolically by

$$P_\infty - S_\infty = P\,(1)$$

* Astrophys Jour, **4**, 91 (August, 1896).
† Nature **55**, 196, 200, 223 (1896)

Runge's Law.

Runge* was the first to point out that the difference between the limits of the D and F series is equal to the wave-number of the first D line (mostly given by $m=2$ in Rydberg's formulæ) This relation is often referred to as Runge's law, and is expressed symbolically by

$$D_\infty - F_\infty = D \quad (2)$$

Thus, in Rydberg's form,

$$F_\infty = N/(2+D)^2, \quad \text{and } F(m) = N/(2+D)^2 - N/(m+F)^2$$

In all series of this type the value of F approximates to unity.

Abbreviated Notation

A convenient and now indispensable abbreviated notation for series was suggested by Ritz in connection with the more complex formula which he employed It is, however, of general application, and merely provides that a term $N/(m+\mu)^2$ or its

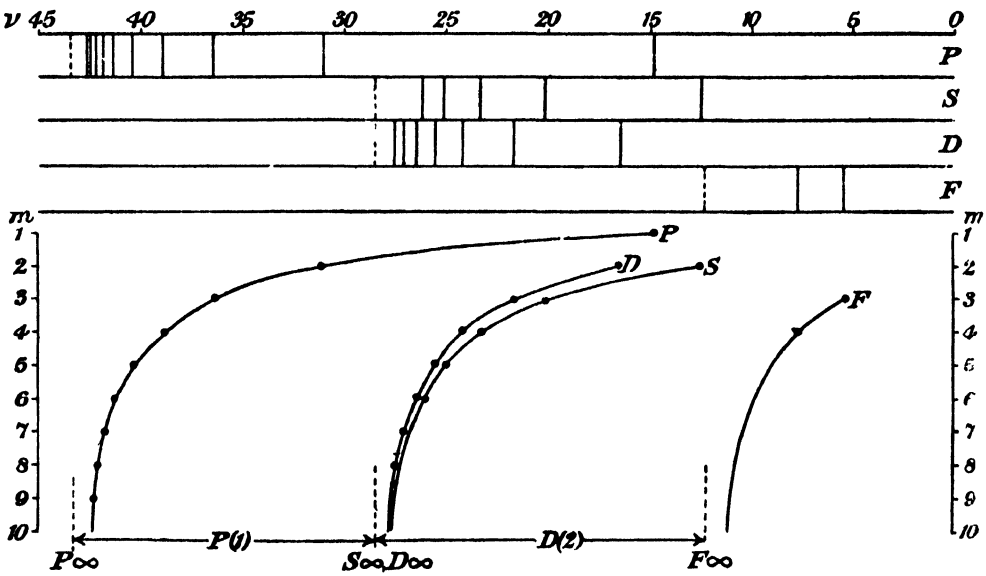


Fig 3.—The Four Chief Series of Lithium

equivalent should be represented by $m\mu$, or by mP, mS, mD, mF in relation to individual series Thus the four chief series are written

$$\begin{aligned} P(m) &= 1S - mP \\ S(m) &= 1P - mS \\ D(m) &= 1P - mD \\ F(m) &= 2D - mF \end{aligned}$$

It is to be understood that while $D(3)$, for example, indicates the *line* in the D series for which $m=3$, $3D$ is equivalent to the *term* $N/(3+D)^2$ and represents the interval from the line $D(3)$ to D_∞.

* Phys Zeit., **9**, 1 (1908)

The foregoing relations, in the case of lithium, are represented graphically in Fig 3, p 17.

In order to distinguish series of different kinds, Paschen designated singlet systems by the use of capital letters, and doublets and triplets by small letters Following a suggestion made by Prof Saunders, however, it will be convenient to adopt Greek letters for doublets, and small letters for triplets Thus

$P,\ S,\ D,\ F$ = Singlet systems.
$\pi,\ \sigma,\ \delta,\ \varphi$ = Doublet ,,
$p,\ s,\ d,\ f$ = Triplet ,,

For general descriptive purposes, however, we shall occasionally use P, S, D, F for any class of series.

Doublet Systems

The special characteristics of a doublet system, such as that of sodium (*see* Plate I), assuming that there are no complications due to satellites, may be briefly stated as follows

(1) In the δ and σ series, the less refrangible components of the pairs are the stronger, and the separations of the components, when expressed in wave-numbers, are constant throughout

(2) In the π series, the more refrangible components of the pairs are the stronger, and the *first* pair has the same separation as δ and σ The components approach each other as the order number increases, and the two series have the same limit.

(3) The φ series consists of single lines

These characteristics are embodied in the following formulæ, where the brighter components are indicated by π_1, σ_1, δ_1, and the fainter by π_2, σ_2, δ_2.—

Rydberg formulæ	Abbreviations	
$\pi_1(m)=N/(1+\sigma)^2-N/(m+\pi_1)^2$	$=1\sigma-m\pi_1$	Shorter λ
$\pi_2(m)=N/(1+\sigma)^2-N/(m+\pi_2)^2$	$=1\sigma-m\pi_2$	Longer λ
$\sigma_1(m)=N/(1+\pi_1)^2-N/(m+\sigma)^2$	$=1\pi_1-m\sigma$	Longer λ
$\sigma_2(m)=N/(1+\pi_2)^2-N/(m+\sigma)^2$	$=1\pi_2-m\sigma$	Shorter λ
$\delta_1(m)=N/(1+\pi_1)^2-N/(m+\delta)^2$	$=1\pi_1-m\delta$	Longer λ
$\delta_2(m)=N/(1+\pi_2)^2-N/(m+\delta)^2$	$=1\pi_2-m\delta$	Shorter λ
$\varphi(m)=N/(2+\delta)^2-N/(m+\varphi)^2$	$=2\delta-m\varphi$	

There is sufficient reason to believe that the relations implied by these formulæ are exact, notwithstanding that the lines composing a series are only imperfectly represented by the simple Rydberg formula The doublet separation is evidently given by $1\pi_2-1\pi_1$

Ritz suggested that the variable part of the formula for the fundamental series might be represented by $m\Delta\pi$, where $\Delta\pi=\pi_2-\pi_1$, or, more fully,

$$m\Delta\pi=N/[m+(\pi_2-\pi_1)]^2$$

The relation, however, is not exact and the fundamental series is now regarded as one of the four chief series of a system, having a certain degree of independence Ritz's form is approximately correct because $\pi_2-\pi_1$ is mostly small, so that $m+(\pi_2-\pi_1)$ is nearly an integer.

Triplet Systems

The characteristics of a triplet system, such as that of magnesium, in which there are no satellites, may be summarised as follows

(1) In the *d* and *s* series the least refrangible component is ordinarily the strongest line and the most refrangible the weakest The wave-number separations are constant for all members of the *d* and *s* series, and the wider separation is that of the two less refrangible members. The wider separation is usually rather more than double the narrower.

(2) In the *p* series, the order of intensities is inverted and the wider separation is on the more refrangible side (usually excepting the first triplet). The series formed of corresponding lines converge to the same limit

(3) The *f* series consists of single lines

Thus, in the abbreviated notation, the four chief series in a system of triplets without satellites are written in the form

$$\left.\begin{array}{lll} p_1(m)=1s-mp_1 & \text{Shorter} & \lambda \\ p_2(m)=1s-mp_2 & & \\ p_3(m)=1s-mp_3 & \text{Longer} & \lambda \end{array}\right\} \text{ or } p\,(m)=1s-mp_i$$

$$\left.\begin{array}{lll} s_1(m)=1p_1-ms & \text{Longer} & \lambda \\ s_2(m)=1p_2-ms & & \\ s_3(m)=1p_3-ms & \text{Shorter} & \lambda \end{array}\right\} \text{ or } s_i(m)=1p_i-ms$$

$$\left.\begin{array}{lll} d_1(m)=1p_1-md & \text{Longer} & \lambda \\ d_2(m)=1p_2-md & & \\ d_3(m)=1p_3-md & \text{Shorter} & \lambda \end{array}\right\} \text{ or } d_i(m)=1p_i-md \quad i=1,2,3$$

$$f\,(m)=2d\ -mf$$

A triplet system, as will appear from the tables, is nearly always accompanied by a system of singlets Combination lines arising from the two systems are found, and it is possible that the singlets form an essential feature of a fully observed triplet system

Satellites

In many spectra the series are rendered more complicated by the presence of *satellites* which accompany some of the chief lines Evidence of the existence of satellites was found by Rydberg, who regarded them as secondary diffuse series, but their true nature was not revealed until Kayser and Runge made their more exact observations of spectra

These satellites are found in connection with doublets and triplets of the diffuse series In doublet series, it is the less refrangible line of each diffuse pair which has a fainter companion or satellite, and the satellite is ordinarily on the side towards the red The brighter component, δ_1, is then displaced from its normal position, and it is the satellite which follows the law of constant separation The chief line approaches the satellite as the order number increases, and the common limit is identical with that of the normal members of the σ_1 series

In a doublet system which includes satellites, the formulæ for the principal and sharp series are unmodified, but the δ formulæ become

$\delta_1'(m)=1\pi_1-m\delta'$ (satellite).
$\delta_1\,(m)=1\pi_1-m\delta$ (first chief line, longer λ).
$\delta_2\,(m)=1\pi_2-m\delta'$ (second chief line, shorter λ).

It will be observed that there will now be two limits for the fundamental series, given by 2δ and $2\delta'$, and consequently the members of this series will be doublets, with a constant separation equal to the separation of the satellite and chief line in the first δ pair (usually given, it must be remembered, by $m=2$) That is

$$\begin{cases} \varphi_1(m) = 2\delta - m\varphi & \text{Brighter, less refrangible component} \\ \varphi_2(m) = 2\delta' - m\varphi & \text{Fainter, more refrangible component.} \end{cases}$$

These relations are shown diagrammatically in Fig. 4*a* An example of a δ pair with satellite appears in the spark spectrum of barium, Plate IV

In a triplet system, the least refrangible components of the diffuse triplets have two satellites, the middle lines one, and the most refrangible components no satellite at all The outer satellite to the first line is the faintest of the group (Fig. 4*b*). It is the satellite to the middle line, and the outer satellite of the least refrangible component which usually show the normal triplet separation given by the sharp series, and the separation of the satellite from the middle line is identical with that of the two satellites to the first chief line (*See also* Pl IIIc)

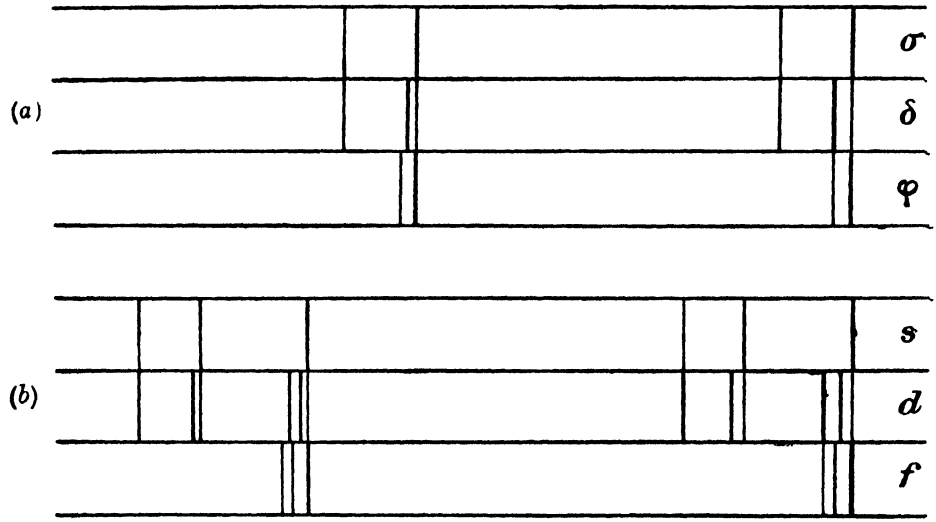


FIG 4.—DIAGRAM ILLUSTRATING ARRANGEMENT OF SATELLITES—(*a*) IN DOUBLET SERIES, (*b*) IN TRIPLET SERIES

With increase of order number the displacements of the chief lines diminish and ultimately vanish. There are thus six series in the *d* group when satellites are present, but there are only three limits, which are identical with the three limits of the *s* series

The formulæ for the diffuse series of triplets thus require the following extensions

		Index numbers
$d_1''(m) = 1p_1 - md''$	Satellites	13
$d_1'(m) = 1p_1 - md'$	Satellites	12
$d_1(m) = 1p_1 - md$	First chief line, longer λ	11
$d_2''(m) = 1p_2 - md''$	Satellite	23
$d_2(m) = 1p_2 - md'$	Second chief line	22
$d_3(m) = 1p_3 - md''$	Third chief line, shorter λ	33

The index numbers suggested by Rydberg, and still sometimes used, are shown on the right. $d(4)_{13}$, for example, would indicate the outer satellite of the first component of the triplet for which $m=4$ in the formula representing the series.

There are now three values of the term $2d$, and therefore three limits for the fundamental series. The fundamental series accordingly consists of narrower triplets in which the separations of the components are constant and equal to those of the first chief line and its two satellites in the first member of the *d* series. Symbolically we have—

$f_1(m)=2d-mf$ Brightest, least refrangible, component.
$f_2(m)=2d'-mf$
$f_3(m)=2d''-mf$ Faintest, most refrangible, component.

As shown in Fig 4*b*, the brightest component and the wider separation are towards the red, as in the *s* and *d* triplets

It is quite possible that satellites are a normal feature of the diffuse series of doublets and triplets, and that their apparent absence in some cases may be due to their small separations from the chief lines.

The probable existence of satellites in some of the fundamental series was first suggested by Hicks In the case of the triplets of strontium and barium they have since been fully established by Saunders from photographs of the arc in vacuo (*see* tables for these elements) The structure of a fundamental triplet having satellites appears to be identical with that of a diffuse triplet, the first line having two satellites and the second line one Additional terms mf' and mf'' thus make their appearance, and the triplet is represented symbolically in the following way.

$$f_1(m)=\begin{cases}2d-nf''\\2d-nf'\\2d-mf\end{cases}\qquad f_2(m)=\begin{cases}2d-mf''\\2d'-mf'\end{cases}\qquad f_3(m)=2d''-mf''$$

The photograph reproduced in Plate III (*b*) shows the details of a fundamental triplet of barium It is from a negative by A S King,* the source of light being an electric furnace containing barium vapour at a low pressure

Negative Wave-numbers.

It has already been explained that the first member of the *S* series is identical with the first of *P*, but is of opposite sign in the respective formulæ In the doublets of the alkali metals, the pair which is common to the two series appears with positive sign in *P* and with negative sign in *S* In the doublets of some elements, however, as in aluminium, the first pair has a positive sign in *S*, and a negative sign in *P*. The first *P* pair then appears to be out of step with the other *P* lines, and the stronger component is on the *less* refrangible side; also the limit of the *P* series is on the red side of the common limit of *D* and *S*, whereas in the alkali doublets it is on the violet side.

It tends to clearness of thought in all such considerations to construct diagrams, as in Fig. 5, showing the negative as well as the positive scale of wave-numbers, and, when the series have been plotted, to imagine the negative members to be folded back into the positive part of the spectrum. This will ensure a proper conception of the appearance which any negative group will present in the actual spectrum

* Astrophys Jour., 48, Plate III (1918).

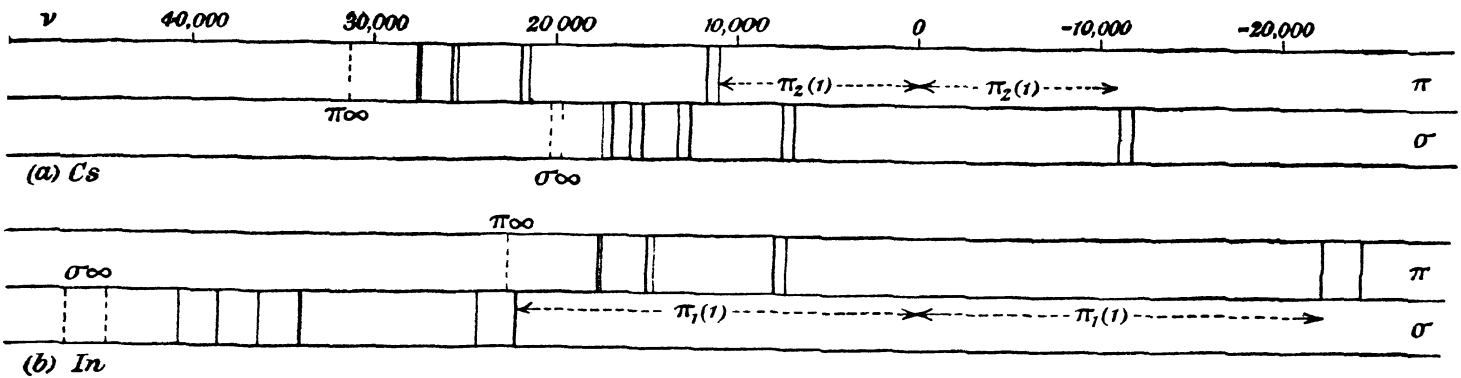


FIG 5 —(*a*) SERIES IN WHICH $P(1)$ IS POSITIVE, (*b*) SERIES IN WHICH $P(1)$ IS NEGATIVE

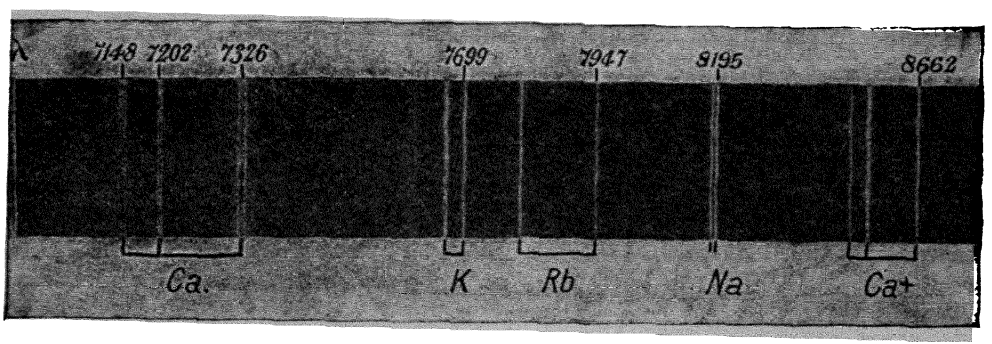


FIG 6 —PHOTOGRAPH SHOWING AN INVERTED DIFFUSE DOUBLET OF IONISED CALCIUM. (λλ8662, 8542, 8498)

A diffuse pair of Na (8195, 8184), the first principal pair of Rb (7947, 7800), and the first principal pair of K (7699, 7665) appear as impurities (Photograph by Col E H Grove-Hills, R E, 1895)

Doublet series with positive and negative $P(1)$ are thus illustrated in Fig 5

When $P(1)$ occurs with negative sign in a triplet series, as is usually the case, the first triplet is inverted, the brightest component and the wider separation being then on the less refrangible side, as in the triplets of the sharp and diffuse series In the remaining triplets, however, the stronger component and wider separation are on the more refrangible side

The first member of the diffuse series also sometimes appears with negative sign, and the corresponding doublet or triplet is then reversed right and left in the actual spectrum An interesting example appears in Fig 6, where the lines 8662, 8542, 8498 of ionised calcium (*see* p 25) form an inverted diffuse doublet with satellite

In the tables which accompany this report negative members are indicated by the usual minus sign The occurrence of these negative signs is probably of no great theoretical importance, because the " terms " from which the lines are derived by taking differences are always positive

The Combination Principle

The possible existence of other series which would be related to the chief series already considered was first suggested by Rydberg,* who pointed out that in his general formula

$$\frac{\nu}{N} = \frac{1}{(m_1+\mu_1)^2} - \frac{1}{(m_2+\mu_2)^2}$$

where m_1 was usually $=1$, it might be supposed very probable that m_1 as well as m_2 would be variable Such variation of m_1 would evidently give rise to other series running parallel to the first Rydberg was unable to establish any such series, but the idea was developed later by Ritz †

The lines of a series always appear as the difference of two terms, one of which is the limit of the series, and the other a " variable part " or " term " of a sequence given by successive integral values of m, the limit itself in the case of the chief series is the first term of the sequence of one of the other series Ritz discovered that lines which were computed by taking differences of other terms of the four chief sequences were often found in the actual spectra, and he called them " combination lines," or " combination series " when more than one line was derived from the same sequence Thus, there might be series $2\,S-mP$, $3\,S-mP$, as well as the chief series, $1\,S-mP$; or $1\,S-mD$, $1\,P-mP$, and so on The fundamental, or " Bergmann," series was at first regarded by Ritz as the combination series, $2D-m\Delta P$, as already explained on p 18, but is now to be considered as one of the chief series

The extensive investigations of infra-red spectra subsequently made by Paschen and his pupils have revealed a very large number of combination lines, and have shown that the combination principle is probably exact The application of this principle has shown that many lines which previously appeared to be unattached really form part of regular systems, of which the principal, sharp, diffuse and fundamental series are the chief members, and it seems possible that in spectra in which series have not yet been identified the complexity may be due to the existence of a great number of combinations

It is interesting to observe that the proof of the combination principle is independent of a knowledge of the true series formula, or even of the exact limits of the various

* Loc cit , p 73.

† Phys Zeit , 9, 521 (1908) , Astrophys Jour , 28, 237 (1908)

series. The limits can, in fact, be determined with considerable accuracy in most cases; but by assuming the Rydberg and Runge laws to be exact, and adopting a limit for one of the series, all the limits will be equally in error Then, if the variable terms *mp*, *ms*, &c , be derived by subtracting the observed wave-numbers of the lines from the adopted limits of their respective series, these terms will be equally affected by any error in the limit first adopted Hence, the errors will cancel each other in taking differences to form the various combinations An example may be taken from lithium (*see* table for this element) by way of illustration The limit calculated for the principal series is 43,486 3, and π (1) is 14,903 8 , thus

$$\begin{aligned} \pi_\infty &= 43{,}486\ 3 = 1\ \sigma && \text{(calculated from actual lines)} \\ \pi(1) &= 14{,}903\ 8 && \text{(observed first principal line)} \\ \therefore\ \sigma_\infty = \delta_\infty &= \overline{28{,}582\ 5} = 1\ \pi && \text{(Rydberg-Schuster law)} \\ \delta(2) &= 16{,}379\ 4 && \text{(observed first diffuse line)} \\ \therefore\ \varphi_\infty &= \overline{12{,}203\ 1} = 2\ \delta && \text{(Runge's law)} \end{aligned}$$

Thus, starting with π_∞, the limits of the other chief series are obtained without independent calculation from the lines themselves The " terms " $m\pi$, $m\sigma$, $m\delta$, $m\varphi$ may then be calculated by subtracting the observed wave-numbers from the limits of the respective series, and such a combination as $2\sigma - 2\pi$ may then be formed as follows .—

$\sigma_\infty = 28{,}582\ 5$	$\pi_\infty = 43{,}486\ 3$
$\sigma(2) = 12{,}302\ 0$	$\pi(2) = 30{,}925\ 9$
$2\sigma = 16{,}280\ 5$	$2\pi = 12{,}560\ 4$

$2\sigma - 2\pi = 3{,}720\ 1$ calculated
$3{,}719\ 9$ observed

If the calculation be repeated with any other value of π_∞, the final result for the combination will be unchanged This not only verifies the general validity of the combination principle, but also indicates the truth of the Rydberg-Schuster and Runge laws, since such calculations are based on the assumption that these laws are true. An exact series formula would doubtless conform with all these relations, but the above procedure renders the calculated combinations independent of a knowledge of the true series formula Including the satellite terms, the possible combinations are very numerous, as will appear from many of the tables for individual elements

Enhanced Line Series

It has been shown by Fowler* that the enhanced lines of helium, magnesium, calcium and strontium form families of series identical in their mutual relationships with those formed by arc lines The enhanced series, however, differ from the ordinary series in the important particular that the series constant takes four times its normal value, so that the approximate formula for such a series would be

$$\nu_E = A - 4N/(m+\mu)^2$$

Hicks has since identified the corresponding series in barium, and other unpublished examples have been found by the author

* Phil Trans , A, 214, 225 (1914).

This feature is obviously of importance in connection with theories of spectra On Bohr's theory, while the ordinary series lines are emitted during the re-formation of atoms from which one electron has been displaced, the enhanced lines are generated when *one* electron returns to an atom from which two electrons have been detached The multiple 4 thus appears as the square of 2 in the theoretical formula for enhanced series

Adopting this interpretation, it has been proposed by Saunders and others that series of enhanced lines should be referred to as series belonging to *ionised* elements—*e g.*, ionised helium, &c The adopted symbol for an ionised element is He^+, Ca^+, &c

Identification of Series

In seeking to arrange lines in series, it is necessary to bear in mind at the outset that lines belonging to the same series have usually the same physical characteristics, and diminish regularly in intensity in passing to the shorter wave-lengths Thus, it frequently happens that lines which form a series can be picked out by inspection of photographs of the spectra, or of maps constructed from tables in such a way as to show the relative intensities of the lines General confirmation may usually be found by drawing a graph with the lines themselves as abscissæ, and successive integers as ordinates, when regularity of the curve would be a strong indication that the lines had been properly allocated A further test might then be made by the calculation of a formula, or by reference to Rydberg's table (Chapter IV)

In the case of doublets and triplets, one would naturally first sort out pairs or triplets of constant wave-number separation, and then try to arrange them in a series system

One of the most valuable tests of the proper allocation of lines in doubtful cases, and especially when only a few lines have been observed, is provided by the behaviour of the lines in a magnetic field , that is, by " Zeeman effects " Preston* was the first to observe that all lines belonging to the same series showed identical magnetic resolutions, not only in type of resolution, but also in wave-number separation of the components Corresponding series in the spectra of several groups of elements were also found to behave in the same way

When the source is viewed at right angles to the direction of the magnetic field, the helium lines all show the " normal triplet " appearance In the case of the sodium lines, D_1 exhibits four components and D_2 six, and exactly similar resolutions are shown by corresponding pairs of the other elements which appear in the same group of the periodic table—namely, K, Rb, Cs, Cu, Ag and Au Further, the same types of resolutions were found by Runge and Paschen for certain pairs in Mg, Ca, Sr, Br and Ra,† and the inference that these belonged to principal series has since been fully confirmed by the observation of other members of the series in the region of short wave-lengths and their connection in series of enhanced lines Pairs of the sharp series show similar resolutions, but in inverse order, in accordance with the Rydberg relationship of the sharp and principal series

Characteristic resolutions have also been observed in the principal and sharp triplet series For the diffuse triplets the resolutions are less simply related, being the same for lines of the same series, but varying in corresponding series of different elements.

* Trans Roy Soc Dublin (2), **7**, 7 (1899).
† Astrophys Jour , **16** 123 (1902), **17**, 232 (1903).

A valuable summary of such observations has been given by Zeeman in his book on " Magneto-Optics "*

Spectra with Constant Differences

In the spectra of many elements in which series of the regular types have not been identified, there are pairs or groups of lines with constant wave-number separations which occur several times This type of regularity was first noted by Kayser† in the spectra of tin, lead, arsenic, antimony, bismuth, palladium, platinum and ruthenium Other examples were found by Rydberg‡ in the red spectrum of argon and in the spectrum of copper The spectra of about 40 elements have since been investigated from this point of view by Emil Paulson § Examples of such constant difference are given in the general tables

The question naturally arises as to whether this kind of spectrum structure represents a second type of regularity, as originally suggested by Kayser, or has its origin in a multitude of combination terms The recent remarkable work of Meissner and Paschen on the spectrum of Neon (*see* Neon) is highly suggestive in this connection, In this spectrum a large number of constant difference groups had been identified, but it has now been found that the lines may be arranged in about 132 series, which are closely inter-related Several of the series run parallel to each other, and thus give rise to pairs or groups with constant differences The individual series are mostly quite normal, but the spectrum differs from those previously described in having several series of each type It would seem possible that other constant-difference spectra may be built up in a similar manner

It is of importance to note that there are spectra which are intermediate between the constant-difference spectra and those which show series of the more usual types Thus, in calcium and strontium (*see* tables) there are constant-difference triplets which have the *same* separations as those falling in the regular series, and pairs having separations equal to one or other of the triplet intervals In copper, on the other hand, the constant-difference pairs and triplets found by Rydberg have no obvious relation to the separations of the pairs which constitute the regular series.

* Macmillan & Co , Ltd (1913), pp 65 and 162

† Handbuch, 2, 573 , Abh , Berlin Akad (1893, 1897).

‡ Astrophys Jour , 6, 239, 338 (1897).

§ Beitrage zur Kenntnis der Linienspektren Diss Lund (1914) Astrophys Jour, 40, 298 (1914), 41, 72 (1915), Y, A Phil Mag , 29, 154 (1915), Pd Ann d Phys , 45, 1203 (1914), La , 46, 698 (1915), Pt Phys Zeit , 15, 892 (1914), Sc , 16, 7 (1915), Gd , 16, 81, Ru , 16, 352, Ru, Nb, Tm , 19, 13 (1918), Ni Zeit Wiss Phot , 18, 202 (1919), Pd, Y

CHAPTER IV.

RYDBERG'S FORMULA.

The Rydberg Constant.

As already pointed out, the Rydberg series constant is derived from the lines of hydrogen, for which the Balmer formula gives

$$N=\frac{4m^2}{m^2-4}\ \nu$$

The wave-lengths of the first six lines as determined on the international scale by W E Curtis * are probably the most accurate at present available for the calculation of N The details are as follows —

Line	m	λ I A	Prob error	λ Vac	ν Vac	N
α	3	6562 793	±0 0017	6564 6022	15233 216	109679 155
β	4	4861 326	0 0010	4862 6797	20564 793	8 896
γ	5	4340 467	0 0006	4341 6830	23032 543	8 776
δ	6	4101 738	0 0013	4102 8915	24373 055	8 748
ε	7	3970 075	0 0016	3971 1940	25181 343	8 738
ζ	8	3889 051	±0 0011	3890 1489	25705 957	8 750

It will be observed that there is a small systematic variation in the values of N yielded by successive lines, the value diminishing as the order number increases, indicating a slight departure from Balmer's law The question is complicated, however, by the fact that the lines are very close doublets ($\Delta\lambda$ in H_α=0 145 A, and in H_β=0 093A)†, in which the less refrangible components are the stronger Curtis's measures refer to the " optical centres of gravity " of these pairs, and it is clear that the simple Balmer formula does not strictly hold for these points It is further probable that neither of the components is exactly represented by the Balmer formula

From an application of the general Rydberg formula, Curtis concludes that the most probable value of N, as determined from the hydrogen lines, is 109,678 3, for wave-numbers on the international scale, corrected to vacuum

Determinations of the value of N from any other series are at present of little weight, as the true form of the series equation remains unknown As an indication of the approximate constancy of N for most series, however, the following values calculated by Paulson‡ by the use of the Ritz formula, to be mentioned later, may be quoted

Lithium	N=109347 5
Sodium	N=109358 5
Potassium	N=110404 5
Rubidium	N=110087 0
Helium	N=109657 2

These values are clearly not inconsistent with a constant N, since the formulæ employed were only approximate

* Proc Roy Soc , A, **90**, 605 (1914) , A **96**, 147 (1919)
† Merton, Proc Roy Soc , A **97**, 307 (1920)
‡ Kongl Fysiog Sallskapets Handl , N F Bd 25, No 12, p 12

It should be noted, however, that Bohr's theory of spectra demands a small variation of N depending upon the atomic weight of the element. (*See* Chapter IX.)

The Constants μ and A

Rydberg pointed out that the most natural method of calculating the constants in his formulæ would be to apply the method of least squares, but he did not consider the data then available to be sufficiently accurate to justify the labour involved. The equation being of the third degree, the least square method is not directly applicable, and it would be necessary first to find approximate values which could be corrected by the more exact method. In fact, it is necessary, or at least useful, to find a set of preliminary values of the constants of the Rydberg formula whatever series equation be adopted.

If two consecutive terms of a series be denoted by ν_m and ν_{m+1},

$$\nu_m = A - \frac{N}{(m+\mu)^2}$$

$$\nu_{m+1} = A - \frac{N}{(m+1+\mu)^2}$$

and

$$\nu_{m+1} - \nu_m = \frac{N}{(m+\mu)^2} - \frac{N}{(m+1+\mu)^2}$$

The value of $(m+\mu)$, and thence of A, can thus be determined by successive approximations, N being taken as 109678·3.

Rydberg's Interpolation Table.—It is more convenient, however, to determine the approximate values of the constants μ and A with the aid of an interpolation table such as was constructed by Rydberg, and then to correct them. This table gives values of the function $N/(m+\mu)^2$ or of $(A-\nu)$, corresponding to values of $(m+\mu)$, ranging from 1·00 to 10·00, together with the differences between consecutive values of the function as m is varied. Rydberg's table was computed with $N=109721·6$, and is still useful, but for the present report new computations to the nearest unit in wave-numbers have been made with Curtis's value of N—namely, 109678·3. The revised functions are given in Table III.

The table will at once give a useful indication as to whether lines suspected of forming a series really do so. Thus, if the interval between two successive lines is 9,057, the table shows that the next line in a normal series would follow after an interval of about 3,676, and the following one after another interval of about 1,846. These would be the intervals if Rydberg's formula were exact, and in practice are only to be taken as indicating the order of magnitude of successive steps from line to line.

But although Rydberg's formula is not exact, the table is almost indispensable in the preliminary calculation of constants when other more accurate formulæ are used. As an example of its use, let two consecutive lines of a series be ν16,226 and ν19,398. The interval between the lines is 3,172, and from the table we find

$$\Delta\nu\ 3{,}184 = \frac{N}{(3·64)^2} - \frac{N}{(4·64)^2} = 8{,}278 - 5{,}094$$

$$\Delta\nu\ 3{,}161 = \frac{N}{(3·65)^2} - \frac{N}{(4·65)^2} = 8{,}233 - 5{,}072$$

Interpolation readily gives

$$\Delta\nu\ 3{,}172 = \frac{N}{(3\ 645)^2} - \frac{N}{(4\ 645)^2} = 8{,}255 - 5{,}083$$

Then

$$A = 16{,}226 + 8{,}255 = 24{,}481$$

or,

$$A = 19{,}398 + 5{,}083 = 24{,}481$$

The approximate equation for the series, therefore, is

$$\nu = 24{,}481 - \frac{N}{(m + 0\ 645)^2}$$

Succeeding members of the series would then be obtained by putting $m=5$, 6, &c., the second terms again being obtained from the table.

As the Rydberg formula does not usually represent a series with an accuracy equal to that of the observations, different pairs of lines may lead to slightly different values of μ and A. In order to distribute the errors, and so get a more even representation of the whole series, Rydberg's procedure was to weight the lines in proportion to the squares of the wave-lengths. It is no longer necessary to do this, as when more than two members of a series are available a more exact formula may be used, such as that of Ritz or Hicks.

The Order Numbers of the Lines

The numeration of the lines when Rydberg's formula is used is by no means a matter of indifference. The numbers actually found by the formula, or from the table, are values of $(m+\mu)$, so that m and μ are not separately determined. To obtain definitive values of m in a system of series Rydberg made use of the relations which he had discovered between the P and S series. Thus the yellow lines of sodium, having the same separation as the pairs of the D and S series, must be $P(1)$, and the order numbers in the P series must be assigned accordingly. The numeration of the lines in S must also be such that $m=1$ in its formula gives a result corresponding approximately with $-P(1)$. The latter criterion is also applicable to singlet series when the first P line occurs in the region covered by the observations. Thus, in the P series of Na, K, Cs, Rb, if $m=1$ is to give the first member, μ must be 1, and in the associated S series $m=1$ will then give $P(1)$ with negative sign, with $\mu<1$, in such systems P_∞ is $> S_\infty$. In many cases, however, as in the triplet series of Mg, Ca, Sr, and in the doublets of Al, $P_\infty < S_\infty$ (*i. e.*, the P series lies on the less refrangible side of D and S), and μ must then be >1 in the formulæ for S in order that $m=1$ may give the first P, $S(1)$ then appears with positive sign, and $P(1)$ has a negative sign as given by $m=1$ in the formula for the P series.

The assignment of the order numbers in the D series remains somewhat arbitrary. Since D and S converge to the same limit, the members of the two series come closer together as the limit is approached, and it would seem most natural to give neighbouring lines the same number in the two series, especially in such cases as potassium, where D and S pairs are nearly coincident in position. In most series the first observed D is given by $m=2$ when this procedure is adopted, and μ is <1. In other series, as in the D triplets of Ca, Sr and Ba, the lines corresponding to $m=1$ also occur in the spectra. When satellites are present, an important indication as to the real first member of the D series is given by the equality of the separation of the satellites and those of the components of the F series.

It should be observed that μ is sometimes rather vaguely regarded as the "phase" of a series, and its values in the series of different elements may be of importance for purposes of comparison in relation to other physical properties of the elements. The correct numeration of the lines determines whether μ is to be taken as greater or less than unity

Enhanced Line Series

The Rydberg interpolation table may also be used for the preliminary calculation of formulæ for enhanced lines, in which the series constant takes the value $4N$ The intervals between the successive wave-numbers are then to be divided by 4 before taking out the values of μ, and in forming the limits of the series the corresponding adjacent terms have first to be multiplied by 4 The following example from a series of enhanced lines of Mg will sufficiently illustrate the procedure —

ν	$\Delta\nu$	$\Delta\nu/4$	$(m+\mu)$	$f(m+\mu)$	$\times 4$	Limit
12,661	10,109	2,527	3 | 0 965	6,976	27,904	40,565
22,770			4 |	4,449	17,796	40,566

The approximate formula would thus be

$$\nu = 40{,}565 - 4N/(m+0\ 965)^2$$

Rydberg's Special Formula

A series of single lines which was identified by Rydberg in the spectrum of magnesium (D in the series tables of Mg) was so imperfectly represented by the ordinary formula that a four-constant formula was adopted—namely,

$$\nu = A - \frac{B}{(m+\mu)^2} - \frac{C}{(m+\mu)^4}$$

where B and C were calculated independently * Other members of the series have since been recorded, however, and it has been found that the series may be at least equally well represented by the formulæ of Ritz and Hicks, involving only three independent constants, and retaining the hydrogen constant N.

It may be noted that the magnesium series in question has not yet been satisfactorily represented by any three-constant formula, and the departure from the formulæ becomes more pronounced in the corresponding singlet series of Ca, Sr and Ba, which belong to the same chemical group.

* Öfversigt af Kongl. Vet.-Akad. Förhandl., Stockholm (1903).

CHAPTER V.

OTHER SERIES FORMULÆ

RUMMEL.

One of the earliest attempts to improve on the Rydberg formula was that made by Rummel,* who employed a formula which may be written

$$\lambda=\lambda_\infty+\frac{C}{(m+\mu)^2-m_0}$$

where λ_∞, C, μ and m_0 are constants special to each series

The same formula, transposed to wave-numbers, was afterwards independently investigated by Fowler and Shaw† in the form

$$\nu=\nu_\infty-\frac{C}{(m+\mu)^2-m_0}$$

and, later, by Halm‡ in the form

$$\frac{1}{\nu_\infty-\nu}=a(m+\mu)^2+b$$

This formula has been shown to represent many individual series with considerable accuracy, but while giving a more convincing proof of the exactness of the laws of limits, it has the disadvantage of not retaining the Rydberg constant, and the calculated line $S(1)$ usually differs widely from $-P(1)$ The formula has, therefore, not much to recommend it, beyond the fact that it admits of an easy direct solution for $(m+\mu)$, and thence for the other constants—namely, that in the second of the above forms—

$$(m_1+\mu)=\sqrt{\frac{a}{a-3}}-1\ 5$$

where $$a=\frac{(\nu_4-\nu_1)(\nu_3-\nu_2)}{(\nu_4-\nu_3)(\nu_2-\nu_1)}$$

and ν_1, ν_2, ν_3, ν_4 refer to four consecutive lines The formula may, therefore, be of occasional use in the determination of limits

Halm has attached some importance to the fact that this formula may be transposed into one which is adapted to the series of lines composing band spectra Thus, if $(m+\mu)$ be put $=0$ in Fowler and Shaw's form of the equation, there results

$$\nu_0=\nu_\infty+\frac{C}{m_0}$$

and, eliminating ν_∞, it is easily shown that

$$\frac{1}{\nu-\nu_0}=\frac{1}{C}\cdot\frac{m_0^2}{(m+\mu)^2}-\frac{m_0}{C}=\frac{\alpha}{(m+\mu)^2}-\beta$$

or, in terms of wave-lengths

$$\frac{1}{\lambda_0-\lambda}=\frac{\alpha'}{(m+\mu')^2}+\beta'$$

* Proc Roy Soc, Victoria, **10**, 75 (1897), **12**, 15 (1899).
† Astrophys Jour, **18**, 21 (1903)
‡ Trans. Roy Soc, Edin, **41**, pt 3, 551 (1905)

The formula represents band series rather better than most of the forms which have been employed, as shown by Halm, and by Fowler in the case of the bands of magnesium hydride.* It is difficult to see, however, what meaning can be attached to such a transposition of the formula

RITZ.

An important modification of Rydberg's formula was made by W. Ritz in 1903 † Ritz's formula was to some extent based upon theoretical considerations and took the general form

$$\pm\nu = N\left(\frac{1}{p^2}-\frac{1}{q^2}\right)$$

where N is the Rydberg constant, and p, q are the roots of certain transcendental equations which are expressible in the form of the semi-convergent series,

$$p=m+\alpha+\frac{\beta}{m^2}+\frac{\gamma}{m^4}+$$

$$q=n+\alpha'+\frac{\beta'}{n^2}+\frac{\gamma'}{n^4}+$$

In the first approximation $p=m+\alpha$, and $q=n+\alpha'$, and the formula becomes identical with that of Rydberg In a second approximation, for a single series, N being constant,

$$\pm\nu=A-\frac{N}{\left(m+\alpha+\frac{\beta}{m^2}\right)^2} \qquad \ldots\ldots\ldots \quad (1)$$

or, in other forms

$$\pm\nu=A-\frac{N}{\left[(m+\alpha)+\frac{b}{(m+\alpha)^2}\right]^2} \qquad \ldots\ldots \quad (2)$$

$$\pm\nu=A-\frac{N}{[m+\alpha'-b'(A-\nu)]^2} \qquad \ldots \quad (3)$$

The numeration of the lines adopted by Ritz was not the same as that of Rydberg In the P series the first line is given by $m=2$, in D by $m=3$, and in S by $m=2.5$

Ritz applied the formulæ (1) and (3) to numerous spectra and showed that they represented the series with much greater accuracy than the three-constant formula of Kayser and Runge The formulæ also have the advantage of retaining the Rydberg constant for all series, and of satisfying the Rydberg relations between the different series with greater accuracy

The formula (3) was considered by Ritz to be the most exact, partly on the ground that extrapolation to $m=1.5$ in the S formula appeared to give a closer approximation to the first P line than the formula (1). It is doubtful, however, whether the superiority over (1) in this respect is general, and the formula is less convenient in practice.

The Ritz formula in the forms (1) and (3) has been largely employed by Paschen

* Phil Trans., A, 209, 460 (1909)

† Ann der Physik., 12, 264 (1903). Phys Zeitschr., 4, 406 (1903). Gesammelte Werke Walther Ritz; Œuvres publiées par la Société Suisse de Physique, Paris (1911).

in his admirable and extensive work on series, and the difference in the numeration of the lines as compared with Rydberg should be carefully noted Thus,

Series	Rydberg	Ritz
P	1, 2, 3	2, 3, 4 .
S	2, 3, 4 .	2 5, 3 5 .
D	2, 3, 4 .	3, 4, 5 .

A consequence of the Ritz numeration is that α is negative, except for series in which the Rydberg figures would give $\mu > 1$ in the *P* and *D* series, or $\mu > 0\ 5$ in the case of the *S* series

The Ritz formula in form (1) has been further tested on some of the series of the alkali metals and of helium by R T Birge,* who found that while the Kayser and Runge formula, even with four undetermined constants, was inadequate, the Ritz formula, with three undetermined constants and a universal constant, was quite satisfactory for substances of low atomic weight The agreement with observation, however, became less accurate with the increase of atomic weight, and left much to be desired in the case of cæsium

The Ritz formula, as pointed out by Birge, has theoretically the form of an infinite series, and the number of terms actually needed to represent a series depends directly upon the magnitudes of the coefficients of the several terms The coefficients are found to increase with increasing atomic weight, and higher terms of the theoretical series become less negligible in the case of the heavier elements The following Table given by Birge in this connection for the *P* series of the elements named is instructive —

Substance	Atomic weight	α	β	*A*
H	1	0	0	27419 7
He	4	0 0111	—0 0047	32033 2
Li	7	—0·047	0 026	43482 1
Na	23	0 144	—0 113	41450 1
K	39	0 287	—0 221	35006 5
Rb	85	0 345	—0 266	33689 1
Cs	133	0 412	—0 333	31394 2

In the case of Na, the Ritz formula was found to represent the *P* series with special accuracy, and to show that for this element the Rydberg-Schuster law was accurately true It should be added, however, that atomic weight is not the only factor which influences the accuracy with which a series may be represented by the Ritz formula, or by formulæ of similar type (*see* Chapter VI).

In a theoretical discussion, Sommerfeld† has arrived at the following generalised form of the Ritz formula .

$$\nu = A - (m, a)$$

where $$(m, a) = A - \nu = \frac{k^2 N}{[(m+a) + \alpha(m, a) + \alpha'(m, a)^2 + \quad]^2}$$

For arc spectra, $k=1$, and for enhanced lines $k=2$ This formula has been applied to several series by E Fues,‡ who also explains a method of determining the constants For the sharp series of singlets of cadmium ($=2P - mS$ in the Ritz-

* Astrophys. Jour , 32, 112 (1910)
† " Atombau und Spectrallinien," 2nd Edition, p 510
‡ Ann d Phys , 63, 21 (1920)

Paschen system), the constants are $A=28843\ 71$, $a=-0\ 077419$, $a=-1{\cdot}41695\times10^{-6}$, $a'=-1{\cdot}70734\times10^{-11}$, $N=109732\ 7$ The lines of the series, with wave-lengths on Rowland's scale, and the differences $O-C$, are as follows.

m	1·5	2 5	3 5	4 5	5 5	6 5	7 5
λ	−2288 10	10395·17	5154 85	4306 98	3981 92	3819	3723
mS	72534 9	19226 4	9449 8	5632 1	3737·3	2666 4	1990 8
$\Delta\lambda$ Paschen	−523	0	0 8	0	−0 36	+0 4	−0 4
$\Delta\lambda$ Fues	0	0	0	+0 02	−0 3	+0 4	−0 3

It will be seen that the additional term gives a marked improvement in the representation of the series About the same accuracy is given by Johanson's formula, to be mentioned later.

Nicholson's Extension of Ritz Formula

The higher terms of the second form of the Ritz formula have been taken into account by Nicholson* in a critical comparison of different formulæ for the lines of helium In this Paper, Nicholson has developed a method of accurately determining the limit of a series having many lines, and has thereby shown that the Rydberg-Schuster law is exact for helium, besides deducing that N has the same value for helium as for hydrogen † Nicholson also concluded that the most accurate form of the series equation is an extension of that of Rydberg, dependent on $(m+\mu)$ and not upon m, namely,

$$\nu=A-\frac{N}{\left[(m+\mu)+\frac{a}{(m+\mu)}+\frac{\beta}{(m+\mu)^2}+\quad\right]^2}$$

Lohuizen

An extensive study of spectral series has been made by Lohuizen,‡ using the formula

$$=A-\frac{N}{(m+\alpha+\beta\nu)^2}$$

It was apparently not recognised that this is equivalent to the Ritz formula no 3

Mogendorff-Hicks

An extensive and critical study of spectral series has been made by Prof W M Hicks in a series of papers communicated chiefly to the Royal Society § The formula which he adopted, while yet unacquainted with the work of Ritz, was

$$\nu=A-\frac{N}{\left(m+\mu+\frac{a}{m}\right)^2}\quad\text{or}\quad\nu=A-\frac{N}{\left(m+\mu+\frac{a}{m}+\frac{\beta}{m^2}\right)^2}$$

* Proc Roy Soc , A, **91**, 255 (1915)

† It is possible that the observations were not of sufficient accuracy to justify this conclusion completely

‡ Bidrage tot de Kennis van Lijnenspectra, Diss Amsterdam (1912), also Kon Akad van Wetenschappen te Amsterdam, June and Sept (1912) (in English)

§ Phil Trans , A, **210**, 57 (1910), **212**, 33 (1912), **213**, 323 (1914), **217**, 361 (1918), **220**, 335 (1920)

This formula was found to give even more accurate results than that of Ritz, and it was rarely necessary to go beyond the a/m term If both α and β are included, β is only a small fraction of α. With α alone the agreement with observation was better than with β alone

The first formula had in fact previously been employed by Mogendorff,* who had applied it successfully to numerous series

As regards the numeration of the lines, Hicks considers it possible, in the case of a well-observed series, to find the correct order numbers by ascertaining the values which represent the series most perfectly when the above formula is used Thus, in the P series of the alkalies the denominator (f denoting a fraction) is $[m+(1+f)-a/m]^2$, and not $(m+f-a/m)^2$, for the latter will not reproduce the series within the limits of observational error, and consequently $\mu>1$, in the S series $\mu<1$ This unique determination of μ is regarded as a matter of the first importance for comparative study, and according to Hicks only fails when the lines are so few, or the measurements so bad, that either a/m or $a/m+1$ will reproduce them within the observational limits It would seem, however, that this criterion is of somewhat restricted applicability

In the case of the S series, it was further found by Hicks that the use of $(m+0\ 5)$ in his formula, in place of m, made it more difficult to fulfil the Rydberg relations between the P and S series, and he consequently adopted integral values throughout Thus in general, the Hicks' numeration is identical with that of Rydberg A special feature of the work of Hicks is the determination of the possible variations in the formulæ constants depending upon the estimated limits of error in the recorded positions of the lines involved

The Hicks formula seems to have been proved by general experience to be even more accurate than that of Ritz, and it is probably the most generally useful formula which has yet been proposed The three-constant form is extremely convenient in practice, and well serves the requirements of most series investigations, that is, it serves sufficiently for the identification of lines belonging to a series, and tends to demonstrate the truth of the Rydberg relations It is not to be expected that it will represent series perfectly There is usually an outstanding error when it is attempted to include the first line of a series, or in extrapolation to negative terms

Paulson

Two formulæ have been tested on certain series by Paulson,† namely

$$\nu=A-\frac{N}{(m+a)^2}\,e^{\frac{b}{m^2}} \quad . \quad . \quad . \quad . \quad . \quad . \quad (A)$$

$$\nu=A-\frac{N}{(m+a)^2}\,e^{\frac{a}{m^2}} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (B)$$

the first having three, and the second two, adjustable constants

Thus, for the D series of lithium, Paulson gives the equations

$$(A) \quad \nu=28588{\cdot}32-\frac{109675\ e^{\frac{0\ 0000631}{m^2}}}{(m+1\ 998672)^2}$$

$$(B) \quad \nu=28593\ 13-\frac{109675\ e^{-\frac{0\ 003497}{m^2}}}{(m-0\ 003497)^2}$$

* Dissertation, Amsterdam (1906).

† Kongl Fysiog Sällsk Handlingar N F, Bd 25, No 12 (1914) (in German)

In (*A*), *m* has the values 1, 2, 3, , and in (*B*) 3, 4, 5, The order of accuracy resulting from the formulæ may be gathered from the appended table, in which the residuals are compared with those given by Lohuizen (Ritz formula), by Kayser and Runge, and by Mogendorff —

m	λ Obs	Δ*A*	Δ*B*	Δ*L*	Δ*K R*	Δ*M*
1 .	6103 77	(0)	(0)	(0)	(0)	(0)
2 . .	4602 37	(0)	(0)	(0)	(0)	(0)
3 .	4132 44	—0 02	+0 31	(0)	(0)	—0 11
4 ...	3915 2	—0 18	+0 28	—0 25	—0 20	(0)
5 .	3794 9	—0 29	+0 24	—0 40	—0 35	+0·09
6	3718 9	—2 16	—1 61	—2 30	—2 25	—1 94
7	3670 6	—1 30	—0 72	—1 45	—1 41	—1 06

It does not seem that Paulson's formulæ have any special advantage over the Ritz' or Hicks' formulæ, and the relation $S(1)=-P(1)$, which is so important in the Rydberg system, has not been taken into consideration

JOHANSON

A study of numerous series has been made by Dr A M Johanson,* using a formula which may be written as follows in the notation adopted in the present report —

$$\nu=A-\frac{N}{\frac{1}{4}[\sqrt{(m+\mu)^2+a}+\sqrt{(m+\mu)^2+b}]^2}$$

It will be seen that if $a=b=0$, and μ is an integer, the formula reduces to that of Balmer for hydrogen, while if μ be a fraction it becomes identical with that of Rydberg When $a=b$, the formula becomes identical with that of Rummel, in the form given by Fowler and Shaw, except that the Rydberg constant N is generally retained Johanson's formula may thus be regarded as a more general form of the Rummel formula For some series the constants a and b have imaginary values

By development in series, Johanson has also shown that the formula includes the formulæ of Kayser and Runge, and Rydberg's more general formula as special cases, and the relation to the formulæ of Ritz and Hicks is also indicated The numeration of the lines in a series begins with zero for the first member

In nearly all cases Johanson has adopted the hydrogen constant for N, and has usually assumed the truth of the Rydberg laws in deducing the limits of series belonging to the same system But in the case of the *D* series of aluminium, which has always been difficult to represent by formulæ adapted to other series, the value of N has been independently calculated, giving the following constants for the less refrangible components —

$N=80858$ $A=48071\ 89$
$\mu=0\ 538853$ $a=17\ 269197$ $b=-0\ 173823$

It is concluded that in this series N cannot have the same value as the Rydberg constant calculated from hydrogen It should be noted, however, that even the five-constant formula does not represent the nine lines of the series with an accuracy equal to that of the observations, the error reaching 0 41 *A* in the case of one of

* Arkiv för Mat, Ast och Fysik, Band 12, No 6 (1917) (in German)

the lines, so that the series can scarcely be used to justify the assumption of a real change in N

In the majority of cases the Johanson formula, with four adjustable constants, appears to be very successful A notable improvement appears in the representation of the diffuse singlet series of magnesium This series was considerably extended by Fowler and Reynolds,* who deduced the following formula from wave-lengths on the Rowland scale* —

$$\nu = 26618\ 20 - \frac{109675}{(m + 0\ 314582 + 0\ 899929/m - 0\ 269730/m^2)^2}$$

Johanson's constants are—

$$A = 26621\ 00 \qquad \mu = 1\ 283559$$
$$a = 4\ 638975 \qquad b = 0\ 281555$$

The respective results from the two formulæ are shown in the following table —

Order number in J	Authority	Limit of Error	λ (Rowland scale)	ν	λ Obs —λ calc	
					F & R	J
0	Paschen	1 00	—17108 1	—5843 61	24903	0 00*
1	Hermann	—	8806 96	11351 59	+142 5	0 00*
2	Rowland	—	5528 641	18082 68	0†	—0 48*
3	,,	—	4703 177	21256 37	0†	+0 55*
4	,,	—	4352 083	22971 14	0†	—0 11
5	F & R	0 02	4167 55	23988 25	—0 1	—0 36
6	,,	0 02	4057 78	24637 17	—0 3	—0 50
7	,,	0 02	3986 94	25074 91	—0 4	—0 54
8	,,	0 03	3938 58	25382 79	—0 4	—0 50
9	,,	0 05	3904 17	25606 50	—0 3	—0 27
10	,,	0 05	3878 73	25774 45	—0 1	—0 08
11	,,	0 10	3859 39	25903 60	0†	+0 11

The lines marked * and † were respectively used in the calculation of constants

It will be seen that Johanson has been able to include the first two lines of the series, and to extrapolate to the 12th member without introducing large errors Paschen, however, does not now consider the first line to belong to the series It is clear, nevertheless, that this series cannot be correctly represented by either of the formulæ It may well be included with the D series of aluminium as among the best examples with which to test any proposed new formula.

Johanson considers that his formula not only gives a good agreement between the calculated and observed wave-numbers for series which have been found to be well represented by other formulæ, but also gives good agreement in other cases, and has the special advantage that lines with the smallest order-numbers may be used in the calculation of limits Also, the change from real to imaginary values of the wave-number given by the formula when m takes the values 1, 0, —1, provides a means of determining the true first line (" grundlinie ") of the series, and thence also the true order-numbers

The method of calculating the constants is indicated in the Paper, but cannot usefully be abstracted The process is less tedious than might be supposed

* Proc Roy Soc A , **89**, 142 (1913).

ISHIWARA

In an extension of Bohr's theory of spectra, J Ishiwara* has deduced a general series formula which, for arc spectra, may be written

$$\nu = A - \frac{N}{(m+\mu)^2[1+\alpha(A-\nu)+\beta(A-\nu)^{\frac{1}{2}}]} - \frac{N\sigma}{(m+\mu)^4}$$

N is the Rydberg constant, adapted for the element as in Bohr's theory (chap IX), and σ is a constant representing $3\pi^2e^4/4c^2h^2$, where e is the unit electric charge, h is Planck's constant, and c is the velocity of light The last term is a relativity correction For enhanced spectra, N and σ are to be multiplied by 4

The formula was applied by Ishiwara to the various enhanced series of magnesium and showed a close agreement with the observations These series are also closely represented by the formulæ of Ritz or Hicks, but in the case of the λ4481 series (with $\beta=0$) there appears to be a definite improvement The formula does not yet appear to have been tested on series of other elements

* Math. and Phys Soc , Tokyo, Series 2, 9, 20 (1916).

CHAPTER VI.

"ABNORMAL" SERIES

Intensities

For the sake of simplicity the foregoing description of the properties of series lines has been restricted chiefly to the most generally occurring cases Some of the rules which have been stated, however, are not of universal application

In general, the intensities show a gradual decrease in passing to the higher members of a series, but there are a few cases in which the sequence of intensities is irregular A well-known example is the very feeble appearance of the second member of the diffuse series of potassium (λ6966), although succeeding pairs decline in regular order The second member of the P singlet series of calcium, λ2721, is also unduly faint as compared with the preceding very intense line at 4227, and the following line at 2398 Other examples are found in the diffuse series of calcium triplets

Satellites

The laws which have been stated with regard to the arrangement of satellites are also sometimes departed from The diffuse series of aluminium provides an example in the case of a doublet series Good measurements of these lines in I A have been made by Grunter,* from which the following may be derived for the wave-numbers of the chief line and satellite, δ_{11} and δ_{12}, and the second line δ_2 —

δ_{12}	$\delta_{11}-\delta_{12}$	δ_{11}	$\delta_2-\delta_{11}$	δ_2
32323 36	1 34	32324 70	112 04	32435 40
38817 13	4 49	38821 62	112 05	38929 18
42121 47	4 05	42125 52	112 03	42233 50
44054 51	2 31	44056 82	112 09	44166 60

The separation of the satellite and chief line does not regularly diminish as in the normal cases, and the constancy of the distance from the satellite to the second chief line shows that it is the first chief line which is irregular, and not the satellite The φ series lies in the infra-red, and the separation of the two components is not known

The recent very complete investigations of the spectra of Ca, Sr and Ba which have been made by Saunders have also shown marked irregularities in the arrangement of the satellites in the diffuse series of these elements (*see* tables)

Spacing of Lines

Another kind of abnormality takes the form of an unusual spacing of the lines of a series, so that the ordinary series formulæ will not represent them with any reasonable approach to the accuracy of the observations The singlet series of magnesium to which reference has already been made (p 37) is one of the best known examples, but more extreme cases have been found by Saunders in the corresponding singlet series of Ca, Sr and Ba The δ series of aluminium doublets and the σ series of thallium are also well-known examples.

* Zeit Wiss Phot, 13, 1 (1914)

Rydberg's simple formula utterly fails to represent such series, and though a great improvement results in some cases from the introduction of another constant, as in the formulæ of Ritz or Hicks, it is evident that some more drastic change in the formula is necessary The study of these extreme cases is clearly of great importance, since very few series can be considered to be perfectly represented by the ordinary formulæ, and if a general formula be possible the abnormal series would seem to provide the most suitable data for its investigation.

The nature of the abnormality will be partially gathered from a comparison with a more normal series, say the *P* singlet series of Ca with the *P* series of He The wave-numbers of the first nine lines of each of these series are given below, together with the values of μ taken from Rydberg's table --

Ca (singlet *P*)				He (doublet *P*)		
m	ν	$\Delta\nu$	μ	ν	$\Delta\nu$	μ
1	23,652			9,231		
		13,080	1 12		16,477	0 939
2	36,732			25,708		
		4,947	1 09		5,652	0 934
3	41,679			31,360		
		2,254	1 14		2,584	0 933
4	43,933			33,944		
		1,492	0 81		1,392	0 932
5	45,425			35,336		
		1,055	0 45		834	0 932
6	46,480			36,170		
		705	0 30		540	0 930
7	47,185			36,710		
		476	0 25		368	0 93
8	47,661			37,078		
		338	0 18		264	0 93
9	47,999			37,342		

It will be seen that in the He series the successive values of μ change very slowly and regularly, whilst in the Ca series they change so rapidly that Rydberg's table would not serve to indicate the positions of succeeding lines with any certainty

The imperfect representation of this series by formulæ will be gathered from the observed *minus* computed wave-numbers given in the accompanying table, the formulæ employed being as follows :—

I $\nu = 49{,}148 - N/[m + 0\,870 + 0\,204/m]^2$

II $\nu = 49{,}216 - N/[m + 0\,345 + 1\,750/m - 1\,024/m^2]^2$

III $\nu = 49{,}305 - 164{,}970/[m + 1\,708666 - 0\,172761/m]^2$

IV $\nu = 49{,}305 - N/[m + 1\,528649 + 2\,774349/m - 1\,190193e^{\frac{1}{m}}]^2$

V $\nu = 49{,}305 - N/[m + 0\,126879 + 6\,620605/m^2 - 5\,679767/m^4]^2$

VI $\nu = 49{,}305 - N/[m - 1\,092198 + 17\,291194/m^2 - 50\,606112/m^4]^2$

VII $\nu = 49{,}305 - N/\frac{1}{2}[\sqrt{(m + 0\,180653)^2 + 23\,351373} + \sqrt{(m + 0\,180653)^2 + 0\,457737}]^2$

VIII. $\nu = 49{,}376 - N/\frac{1}{2}[\sqrt{(m + 0\,100167)^2 + 23\,882095} + \sqrt{(m + 0\,100167)^2 + 0\,564884}]^2$

The limit given by Saunders (49,305) has been adopted in all but the first two and the last formulæ, and in all cases the lines used in the calculation of constants

are marked by an * In III., N has been independently calculated In VI, the lines have been numbered 2, 3, 4 in place of 1, 2, 3 Formula IV was suggested by the forms first used by Paschen for certain series in the spectrum of neon, none of which, however, appear to be adapted to the Ca series under discussion Paschen afterwards found that such formulæ were not required for the neon series The last two formulæ are in Johanson's form, one with the limit assumed, and the other with the limit calculated

Calcium, Singlet P Series

m	λ	ν	I	II	III	IV	V	VI †	VII §	VIII §
1	4226 73	23652	+2*	+8*	0*	0*	*	0*	0*	0*
2	2721 65	36732	+1*	0*	0*	0*	−3234	−1892	−1642	−1735
3	2398 58	41679	−397	0*	0*	0*	*	+6*	0*	0*
4	2275 49	43933	−686	−357	−232	−394	*	0*	0*	0*
5	2200 76	45425	−584	−361	−176	−303	−92	−44	+6	−8
6	2150 78	46480	−367	−223	− 28	−244	−67	−6	+71	+42
7	2118 68	47185	−205	−119	+ 68	−197	−39	+16	+98	+59
8	2097 49	47661	−101	−54	+114	−135	−24	+22	+99	+51
9	2082 73	47999	−28	−8	+138	−92	−12	+26	+93	+40
10	2073 04	48223	0*	0*	+125	−85	−25	+5	+62	+5*
11	2064 77	48416	+44	+30	+135	−56	−12	+13	+63	−2

† Numeration begins with $m=2$

§ Numeration begins with $m=0$, and for the first line the *difference* of the two terms inside th ackets has to be taken

The results of the calculations do not clearly suggest that the necessary modification of the ordinary formulæ is to be found in a change of the value of the series constant As already remarked, however, in the case of the d series of aluminium, Johanson found it impossible to represent the lines by his formula without making such a change, he deduced a value of about 80,000 for this series in place of the usual 109,678, and found a fair representation of the lines The constant a in the formula then had the very large value 17 3, as compared with values which rarely exceed 2 for most series, while b was small Ca P has the same features in greater degree

A part of the difficulty of representing an abnormal series such as that of the Ca P singlets appears to arise from a difference in the rates of convergence of the earlier and later lines Lorenser* and Saunders have illustrated this as in Fig 7 If the series equation be of the form

$$\nu = A - \frac{N}{[m+\mu+f(m)]^2}$$

we have

$$f(m) = \sqrt{\frac{N}{A-\nu}} - (m+\mu)$$

If N be assumed, and a value of A be assigned from a consideration of the later lines of the series, $f(m)$ will represent what Saunders has called "the residual," and the curve is drawn by plotting the residual, or $\mu+f(m)$ against m It will be seen that the curve has a point of inflexion in the part corresponding to the earlier members, so that the residual cannot be a very simple function of m

* Beitrage zur Kenntnis den Bogenspektren der Erdalkalien Dissertation, Tubingen (1913) p 41.

The curve represents the Ca singlet P series, A having been taken as 49,305 the values of $\mu+f(m)$ for the eleven lines are

(1) 1 0677	(7) 0 1927
(2) 0 9535	(8) 0 1679
(3) 0 7924	(9) 0 1641
(4) 0 5185	(10) 0 0681
(5) 0 3167	(11) 0 1073
(6) 0 2309	

Similar results are shown also by the corresponding singlet series of strontium and barium, and also for the d series of calcium triplets and the f series of barium, particulars of which will be found in the general tables

It will be evident that the representation of series by formulæ is a subject which is far from having been exhausted, and that the "abnormal" series to which

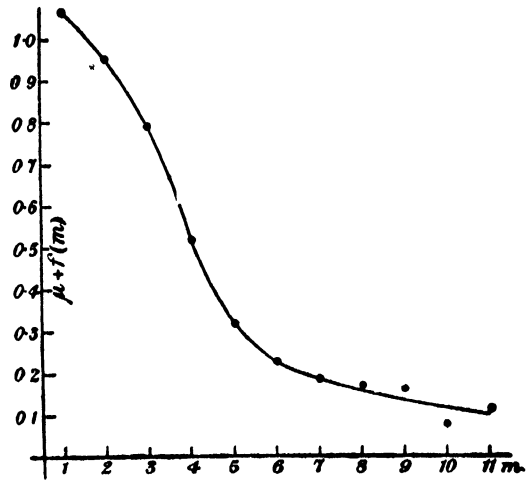


FIG 7.—CURVE OF $\mu+f(m)$ FOR THE Ca SINGLET PRINCIPAL SERIES

attention has been directed furnish valuable material for further investigations The simpler formulæ which represent many of the series very closely are evidently only approximate, and cease to be of use in extreme cases They would seem to be merely first approximations to a more general formula which may be applicable to all series. Until some such formula has been found, it would seem that some interesting questions, such as that of the approximate constancy of N for different elements, cannot be completely investigated

Meanwhile, in investigations connected with combination series, as already explained, the use of a formula can be dispensed with The limit of one of the main series having been calculated, the other limits are derived by the Rydberg-Schuster and Runge laws, and "terms" are formed for the lines by subtracting the wave-numbers from the limits of the series to which they belong The combinations of the terms may then be compared with the wave-numbers of other observed lines

CHAPTER VII.

SPECTRA AND ATOMIC CONSTANTS

General Relationships

Following the classification of spectral lines in series, it was natural to seek for relations between the series spectra of different elements Hartley* and others had, in fact, previously noted similarities in the spectra of related elements, such that one spectrum might to some extent be considered to be produced by displacing another bodily through a certain distance It is interesting to note that in this connection Hartley found " a considerable body of evidence in support of the view that elements whose atomic weights differ by a constant quantity, and whose chemical character is similar, are truly homologous , or, in other words, are the same kind of matter in different states of condensation "

The early work of Rydberg, and that of Kayser and Runge, indicated two definite influences of atomic weight upon the respective series spectra —

(1) In elements of the same chemical group, the limits of corresponding series advance towards the red with increasing atomic weight

(2) In elements of the same group, the wave-number separations of doublets or triplets in corresponding series are roughly proportional to the squares of the atomic weights

These results are illustrated diagrammatically for the sharp triplet series of Mg, Ca, Sr and Ba in Fig 8

Rydberg also drew attention to the approximate constancy of the sums of the constants μ in his formulæ for the sharp and diffuse series in the spectra of elements of the same group and of their differences in corresponding elements of Groups II and III These relations, however, are very rough, and a similar examination of the constants of the Hicks formulæ has not led to any significant results

Limits and Atomic Weights

The general relation between the limits of corresponding series in elements of the same group is illustrated in the following table —

Doublets	π_∞	$\sigma_{1\infty}$	Triplets	p_∞	s_∞	Triplets	p_∞	$s_{1\infty}$
Li	43,486	28,582	O	36 069	23,206	Mg	20,474	39,760
Na	41,449	24,476	S .	31,148	20,085	Ca	17,765	33,989
K .. .	35,006	21,963	Se	30,699	19,268	Sr	16,898	31,038
Rb .	33,089	20,873				Ba	15,869	28,515
Cs .	31,405	19,672						

In the case of the alkali metals, if the limits of the subordinate series and the atomic weights be taken as co-ordinates, the points lie on a fairly regular curve, except as regards K , or, if the logarithms of the two sets of figures be plotted, the points will lie nearly on a straight line, with K again out of order. The Ca group shows similar results, with Ca discordant.

The limits of the principal series, however, are less regularly connected with the atomic weights than those of the subordinate series

* Jour. Chem. Soc , 43, 390

Limits and Atomic Volumes

A possible relation between the limits of the subordinate series and the atomic volumes of the elements appears to have been first suggested by Reinganum * If the atomic volumes of the elements of Group II were divided by 4, and those of Group III by 6, while those of Group I retained their ordinary values, Reinganum found that when the logs of the modified atomic volumes were plotted against the logs of the limits of corresponding series, the points for *all* the elements considered fell approximately on a straight line The relation, however, is by no means precise

From the consideration that the wave-frequencies of the transverse vibrations of an elastic body are inversely proportional to the linear dimensions (or to the cube roots of the volumes), and that some similar relationship might be found for vibrating atoms, Halm† also suggested a possible relation between the limits of series and the

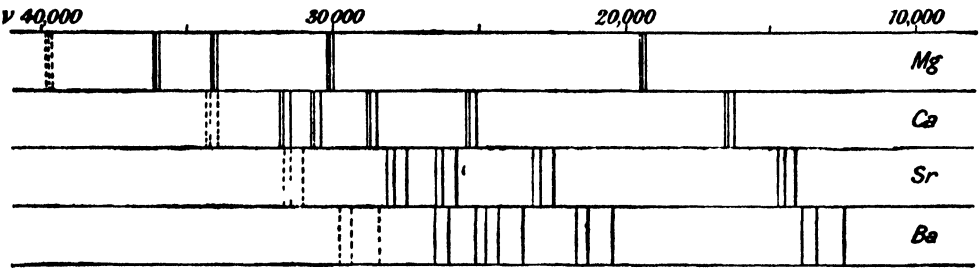


Fig 8 —The Sharp Series of Mg, Ca, Sr, Ba, showing Influence of Atomic Weight

atomic volumes of the elements For elements of the same group, Halm found that the limits of the subordinate series were approximately represented by an equation of the form

$$S_\infty = a + bv^{-\frac{1}{3}}$$

where v is the atomic volume and a and b are constants Thus, the alkali group was represented with $a=9{,}934$, $b=42{,}300$, Zn, Cd, Hg with $a=24{,}228$, $b=38{,}960$, and so on The approximate relation, however, was not fulfilled for the group Al, In, Tl As in the case of the atomic weights, the limits of the principal series of the alkalies failed to show the same simplicity as those of the subordinate series, a fair agreement, however, was obtained by making $a=34{,}610$ and $b=2\times10^4$ for Li and Na, and $a=12{,}758$, $b=8\times10^4$ for K, Rb, Cs

The possible atomic volume relationship has also been considered by Birge,‡ who found that the constants of the Ritz formulæ for the principal series of the alkali metals were roughly proportional to the atomic volumes, as shown in the following table —

Element	a	b	b/a	At vol	a/at vol	b/at vol
Na	0 14433	—0 11302	0 784	23 606	613×10^{-5}	480×10^{-5}
K	0 28692	—0 22083	0 770	44 617	642×10^{-5}	495×10^{-5}
Rb	0 34559	—0 26577	0 768	56 05	627×10^{-5}	473×10^{-5}
Cs	0 41196	—0 33269	0 807	70 584	585×10^{-5}	472×10^{-5}

* Phys Zeit, **5**, 302 (1904).
† Trans Roy Soc, Edin, **41**, 593 (1905).
‡ Astrophys Jour, **32**, 123 (1910)

It is doubtful if anything more significant is to be gained from comparisons of the formulæ constants than from direct discussions of the limits of the subordinate series, since the latter are determined by the constants of the principal series

In the case of the alkali metals, there is certainly a great improvement in the representation of potassium when atomic volumes are substituted for atomic weights in the construction of a curve showing the relation with the limits of the subordinate series In the alkaline-earth group, however, strontium is notably discordant, as may be observed by plotting the following figures —

Element	$s_{1\infty}$	At vol
Mg	39 752	14 0
Ca	33,983	25 5
Sr	31,026	34 5
Ba	28 575	36 63

Further data for the consideration of these questions may be derived from the general tables of spectra which form part of this Report

Doublet and Triplet Separations

The following extract from a table given by Rydberg* will illustrate the approximate relation between the separations of doublets and triplets and the squares of atomic weights in elements of the same group †

	At wt	$\Delta\nu$ or Δ_{1}	$10^3\Delta_1/W^2$		At wt	$\Delta\nu$	$10^3\Delta\nu/W^2$
Li	7 03	—	—	Cu	63 44	248 54	61 8
Na	23 06	17 19	32 3	Ag	107 94	920 48	79 0
K	39 14	57 85	37 8	Au	197 25	3815 40	98 1
Rb	85 44	235 98	32 3				
Cs	132 88	553 87	31 6	Al	27 08	112 02	152 8
				Ga	69 9	823 6	168 6
Zn	65 38	388 97	91 0	In	113 4	2212 54	172 1
Cd	112 08	1170 76	93 2	Tl	204 15	7792 63	187 0
Hg	200 36	4631 17	115 4				

It will be seen that the proportionality between $\Delta\nu$ and W^2 in the same group is only very roughly given by the equation

$$\Delta\nu = kW^2, \text{ or } W = c(\Delta\nu)^{\frac{1}{2}}$$

A closer agreement was found by Runge and Precht§ by using the equation

$$W = C(\Delta\nu)^n$$
$$\text{or } \log W = \log C + n \log (\Delta\nu)$$

Thus, it was found that by taking logs of the atomic weights and logs of the separations as co-ordinates, the points representing elements of the same group lie nearly on a straight line In an attempt to determine the atomic weight of radium from the spectroscopic data, Runge and Precht discussed the enhanced doublets of the calcium group, for which the equation becomes

$$\log W = 0\ 2005 + 0\ 5997 \log \Delta\nu$$

* Rapp au Congrès Int de Phys , Paris (1900).

† Note —Rydberg and some other writers have represented separations by ν, but, as this is more appropriate to wave-numbers, $\Delta\nu$ is here adopted for the separations of doublets and triplets.

‡ The separation 0 34 given by Kent is out of step with $\Delta\nu$ for the other alkali metals

§ Phys Zeit, **4**, 285 (1903) , Phil Mag , **5**, 476 (1903)

The results are shown in the following table —

	$\Delta\nu$	W	W calc	$O-C$
Mg	91 7	24 36	23 84	+0 52
Ca	223 0	40 1	40 6	−0 5
Sr	801 0	87 6	87 5	+0 1
Ba	1691 0	137 4	136 9	+0 5
Ra	4858 5	225 0	258 0	−33 0

The result for Ra is much too high, and it is evident that the formula is not sufficiently exact for the long extrapolation required A variation in procedure was adopted by Rudorf,* who plotted curves for the different groups with $10\Delta\nu/W^2$ and W as co-ordinates The curves were rather complex, but appeared to pass in all cases through the zero point No calculations were given, and the method does not appear to lend itself to such an extrapolation as that required for radium

Using Runge and Precht's data, Dr Marshall Watts† derived an interpolation formula for the enhanced doublets of the calcium group, namely,

$$\log W = 1\,886242 + 0\,623179a - 0\,080391a^3 - 0\,0374175a^4$$

where $$a = \log \Delta\nu - 2\,813121$$

The calculated atomic weights were Mg 24 32, Ca 40 08, Sr 87 62, Ba 137 41, Ra 226 56, in close agreement with the true values It will be observed, however, that the formula involves as many constants as there are elements in the group

A further attempt to determine the atomic weight of radium was made by the Misses Anslow and Howell,‡ using the separations of the extreme members of triplets which they believed they had identified in radium, and comparing them with corresponding terms for other elements of the group The logs of the separations and logs of the atomic weights gave points which lay very nearly on a straight line, and indicated 231 7 for the atomic weight of radium

The separations of doublets and triplets were discussed by Ritz in a different way § Thus, the main separation in a doublet system in our notation is given by $\sigma_2\infty - \sigma_1\infty$, and from the relation between the σ and π series we have

$$\Delta\nu = \sigma_2\infty - \sigma_1\infty = N/(1+\pi_2)^2 - N/(1+\pi_1)^2$$

where π_2 and π_1 may include extra terms introduced for the better representation of the series In the Ritz formulæ, the denominator terms are indicated by $(m+p_1+\pi'/m^2)$ and $(m+p_2+\pi''/m^2)$, and Ritz found that the quantities (p_1-p_2) gave a much smaller range of values in relation to the squares of the atomic weights than did the separations themselves when different groups of elements were included in the comparison His results are shown in the following table —

	Na	K	Rb	Cs	Cu	Ag	Mg	Ca	Sr	Zn	Cd	Hg	Al	In	Tl	He
$\Delta\nu_1\ 10^3/W^2$	32 3	37 8	32 2	31 6	61 8	79 0	68 8	66 1	51 5	91 0	93 2	115 4	152 8	172 1	187·0	63 8
$\frac{p_1-p_2}{W^2}\ 10^7$	14 2	18 9	18 0	18 6	18 6	24 2	14 6	17 7	15 7	17 2	18 6	22 3	24 8	29 2	32·7	20 4

* Zeit Phys Chem , **50**, 100 (1904)
† Phil Mag , **18**, 411 (1909)
‡ Proc Nat Acad Sci , Wash , **3**, 409 (1917)
§ Astrophys Jour , **28**, 241 (1908) , **29**, 243 (1909).

The essential difference of procedure as compared with the use of direct values of $\Delta\nu$ is that in the form (p_1-p_2) the doublet or triplet separations are associated with the limits of the subordinate series Ritz regarded these results as merely preliminary, but does not appear to have carried the matter further A more exhaustive study, however, has been made by Hicks (*see* Chapter VIII)

The results obtained by substituting atomic volumes for atomic weights in relation to the doublet and triplet separations in the foregoing comparisons do not appear to be any more definite than those already quoted Thus, in the elements of the alkali group, potassium still deviates from the curve which connects atomic volumes with the separations, or from the straight line when the logarithms are plotted.

Homologous Lines and Atomic Weights

In an attempt to discover the relations between the spectra and other physical properties of the elements, Ramage* compared graphically the corresponding or " homologous " lines in the different elements of the various groups The characteristic flame lines Mg 2852, Ca 4227, Sr 4607, Ba 5535, are examples of such lines; and, in general, lines of corresponding series which have the same value of m would be regarded as homologous Such lines, like the limits of the series to which they belong, usually advance towards the red with increase of atomic weight The curves connecting their wave-numbers with the atomic weights, or with the squares of the atomic weights, however, were found by Ramage not to be continuous throughout the whole of a group of elements In the alkalies, for instance, there was a break between Na and K It does not seem probable that the discussion of individual lines will lead to more definite relations than those of the limits of the series

Ramage also derived empirical formulæ for the series of K, Rb and Cs, in which the atomic weight was the only variable, apart from the parameter m Thus, he found that the second components of the principal series were given by

$$\nu=35{,}349-0\,2233W^2-N/[m+1\,19126+0\,00103W \\ +(0\,04377+13W^2\times10^{-7})(1-3^{1-m})]^2$$

The possibility of obtaining such a formula strongly suggested to Ramage that the differences between the series of the three elements in question depended solely upon differences of atomic weights The number of constants involved, however, is too large to give confidence in such a conclusion, especially as the formula fails to include lithium and sodium

Other relationships between homologous lines and atomic weights were afterwards suggested by Marshall Watts † Thus, in each of the two groups K, Rb, Cs, and Ca, Sr, Ba, the differences of wave numbers between corresponding lines in their spectra were found to be nearly proportional to the differences between the squares of the atomic weights In the first group the lines having the following wave-numbers were assumed to be homologous —

	Cs		Rb		K
(*a*)	12,469 (6)	...	13,742 (4)	.	14,465 (7)
(*b*)	21,764 (6)	...	23,714 (6)	...	24,700 (6)
(*c*)	21,945 (8)	...	23,791 (8)	...	24,719 (8)
	&c		&c		&c

* Proc Roy Soc , **70**, 1 and 303 (1901-02).
† Phil Mag , (6) **5**, 203 (1902).

Adopting atomic weights 132 7 for Cs and 39 9 for K, the rule gives with lines (*a*) 86 87, with lines (*b*) 83 24, and with lines (*c*) 83 11 for the atomic weight of Rb (85 2) The limits of the principal series, treated in the same manner, give 86 0 Reference to the general tables will show that the lines (*a*) are not homologous, and if the correct line of Cs(13,138) be introduced the deduced atomic weight for Rb becomes 102 The suggested relation also excludes lithium and sodium and would therefore seem to have no great significance.

In another class of elements, represented by Zn, Cd, Hg and Ga, In, Watts found that the differences between the wave-numbers of certain lines of one element were to the differences between the corresponding lines of the other elements as the squares of their atomic weights Among the pairs of assumed corresponding lines of Cd and Zn given by Watts are the following —

	Cd	Zn
(*a*)	30654 4 (10)	32500 0 (8)
(*b*)	30734 9 (8)	32540 1 (10)
(*c*)	31905 5 (8)	32928 7 (10)
(*d*)	32446 8 (6)	33118 6 (8)
	&c	&c

The assumption of 111 83 for the atomic weight of Cd then gives 65 44 from (*a*) and (*c*), 65 69 from (*a*) and (*d*), and so on, for that of Zn (64 9) Since lines (*b*), (*c*) and (*d*) belong to corresponding triplets, and lines (*a*) are not placed in series, it will be seen that in place of taking the triplet separations themselves to be proportional to the squares of the atomic weights, Watts has added wave-numbers to the separations equal to the intervals between the lines (*a*) and (*b*) of the two elements That is, since $(c)-(b)=\Delta\nu_1$, and $(d)-(c)=\Delta\nu_2$, if $(b)-(a)$ be called x for Cd and y for Zn, Watts makes—

For (*a*) and (*c*) $$\frac{x+\Delta\nu_1}{y+\Delta\nu_1'}=\frac{(\mathrm{Cd})^2}{(\mathrm{Zn})^2}$$

and for (*a*) and (*d*) $$\frac{x+\Delta\nu_1+\Delta\nu_2}{y+\Delta\nu_1'+\Delta\nu_2'}=\frac{(\mathrm{Cd})^2}{(\mathrm{Zn})^2}$$

The difference between the two results from members of undoubtedly corresponding triplets, measured with sufficient accuracy in each case, sufficiently indicates that this mode of correcting the triplet separations in forming the ratio of squares of atomic weights cannot be valid. In fact, the two expressions on the left could only be equal if $\Delta\nu_2/\Delta\nu_2'$ were also equal $(\mathrm{Cd})^2/(\mathrm{Zn})^2$, and this is only approximately true for these two elements, and very far from true when mercury is taken as one of the elements Some of the other lines taken to be homologous by Watts are certainly not corresponding lines, and it is difficult to understand on what principle they were selected The deduced values for Zn range from 64 77 to 67 08

Separations and Atomic Numbers

Since atomic numbers probably determine the places of the elements in the periodic table more correctly than the atomic weights, several attempts have been made to correlate these numbers with the series spectra.

In a graphical repetition of Runge and Precht's work on the doublet separations

in the calcium group Ives and Stuhlmann* found that the results were somewhat more consistent than for the atomic weights, but the atomic number derived for radium was 96, in place of the true value 88 Using the wave-number differences between extreme members of the triplets occurring in elements of the same group, it was found also by Anslow and Howell† that when the logarithms of these differences were plotted against the logarithms of the atomic numbers, the points fell more accurately on a straight line than with atomic weights, and an atomic number of 87 was deduced for radium

Separations in relation to atomic numbers have also been discussed by H. Bell,‡ who employed two formulæ, namely —

$$(1)\ \sqrt{\Delta\nu}=m(N-N_0)\,, \qquad (2)\ \log \Delta\nu=p \log N+q$$

where $\Delta\nu$ is the separation, N the atomic number, and the other terms are constants to be calculated for each group of elements The figures for the alkali group will serve for illustration —

	At No	$\Delta\nu$ obs	$\Delta\nu$ calc (1)	$\Delta\nu$ calc (2)
Li .	3	0 34§	0 25	1 03
Na	11	17 21	16 48	17 21
K	19	57 90	58 0	56 17
Rb	37	237 71	244 0	237 7
Cs .	55	564 10	558 3	560 8

$m=0\ 4447$, $N_0=1\ 875$, $p=2\ 1645$, $q=-1\ 01832$

A somewhat similar formula was tested by Paulson,‖ namely

$$\log \Delta\nu=A \log (N+n)+B$$

where N is the atomic number, $\Delta\nu$ the separation, A and B constants, and n a positive or negative integer For each group of elements the value of n was first determined graphically, and the constants A and B were then calculated by the method of least squares The atomic numbers used were those of Rydberg's system,¶ which are two units higher than those of Moseley The nature of Paulson's results may be gathered from the following data for the triplets of the calcium group —

$$\log \Delta\nu_1=2\ 163129 \log N-0\ 871542$$
$$\log \Delta\nu_2=1\ 748748 \log (N-4)-0\ 459734$$

	N (Rydberg)	$\Delta\nu_1$	$\Delta\nu_2$	$\Delta\nu_1$ calc	$O-C$	$\Delta\nu_2$ calc	$O-C$
Mg ..	14	40 92	19 89	40 52	+0 40	19 45	+0 44
Ca ..	22	105 99	52 11	107 72	−1 73	54 38	− 2 27
Sr .	40	394 44	187 05	392 57	+1 87	182 74	+ 4 31
Ba .	58	878 4	370 3	876 96	+1 44	371 35	−1 05
Ra	90	—	—	(2268)	—	(838)	--

The extrapolation to radium does not agree at all closely with the separations 2016 64 and 1036 15 afterwards suggested by Anslow and Howell It will be observed

* Phys Rev , 5, 368 (1915).
† Loc cit.
‡ Phil Mag , (6) 36, 337 (1918)
§ Not used in calculation of constants
‖ Astrophys Jour , 49, 276 (1919)
¶ Jour Ch Phys , 12, No 5 (1914).

that no simple connection between the atomic numbers and the doublet or triplet separations has yet been discovered.

There does not appear to be any published record of investigations of the limits of series in relation to atomic numbers, but a few trials will show that the results are generally similar, and not more exact, than for the atomic weights. Thus, in the alkali group, potassium remains decidedly discordant, and in the calcium group, calcium again shows considerable departure from the approximate regularity shown by the other four elements. When the limits of the principal series are plotted against atomic numbers the points show the same absence of simple regularity which was found with the atomic weights.

Conclusions

These results are in a sense disappointing. It would seem that the spectra must for the present be regarded as constants of the elements which show no simpler relation to other constants than is shown by some of the constants among themselves. Thus, in the alkali group, the curve connecting atomic weights with melting points, or that connecting atomic weights and atomic volumes, is closely similar to that relating the limits of the subordinate series to atomic weights, and a similar discrepancy is shown by potassium in each case. Again, there is no simple relation between the atomic weights and densities in this group of elements, just as there is no simple law connecting the limits of the principal series. It can only be concluded that although the spectra change progressively with atomic weights, atomic volumes or atomic numbers, the laws governing the changes are not clearly indicated by any of the foregoing investigations.

CHAPTER VIII

THE WORK OF HICKS.

The discussion of spectral series which has been made by Prof W M Hicks* is of so special a character that it is most conveniently treated separately The investigation covers a great deal of ground, and it will only be possible to attempt to give a general idea of some of the methods employed In the earlier papers Hicks proves the value of the series formula

$$\nu = A - \frac{N}{\left(m+\mu+\frac{\alpha}{m}\right)^2}$$

and makes a special feature of calculating the influence of possible errors of observation on the values of the constants for the different series Having determined the constants for many of the known series, he proceeds to discuss them in relation to the atomic volumes and atomic weights of the respective elements The adopted wave-lengths are on Rowland's scale, and as the conclusions would not be modified by the substitution of wave-lengths on the international scale, it has not been thought necessary to recompute the formula constants and the quantities which depend upon them

It should be remarked that in some of his papers Hicks departs from the more usual practice, and writes, for example, p(1), instead of 1 p, for the variable part or " term " of the first principal line

Atomic Volumes

Among the more striking results obtained by Hicks in his first paper is the following comparison of the constants for the stronger components of the principal series of the alkali metals with the atomic volumes The limits of the series are also entered for completeness

	μ	α	$\mu-1$	$\mu-1+\alpha$	At vol	Limit
Li	0 951609	+0 007365			1×11 81	43,486
Na . .	1 148678	—0 031776	2×0 074339	2×0 058451	2×11 80	41,449
K	1 296480	—0 062511	4×0 074120	4×0 058492	4×11 15	35,006
Rb	1 366399	—0 074554	5×0 073280	5×0 058369	5×11 21	33,689
Cs	1 450967	—0 090077	6×0 075161	6×0 060148	6×11 76	31,405

The constants $(\mu-1)$ and $(\mu-1+\alpha)$ are thus approximately integral multiples of constant numbers, and the atomic volumes the same multiples of another number. Lithium is excluded in this mode of treating the formula constants, and Hicks has suggested that what is usually regarded as the principal series of lithium may really be a combination $1s-md$ or $1s-mf$, the easy reversal of the lines, and the similarity to the principal series of the other alkali elements, however, is directly opposed to this supposition Assuming the above relation to be sufficiently general, and observing that $\alpha/(\mu-1)$ is nearly constant, Hicks endeavoured to bring the figures into closer agreement by the introduction of an atomic weight term as a correction to μ (*I* 79).

* I, Phil Trans, A **210**, 57-111 (1910), II, **212**, 33-73 (1912), III, **213**, 323-420 (1914), IV, **217**, 361-410 (1917), V, **220**, 335-468 (1919) Corresponding numbers are used for references to these papers in the text

Atomic Weight Term

The atomic weight term, as defined by Hicks, depends jointly upon the separations of doublets or triplets, and the limits of the subordinate series Thus, if D represents denominator, the formulae for the two members of a sharp series of doublets may be written

$$\sigma_1(m)=N/D_1^2-N/D_m^2$$
$$\sigma_2(m)=N/(D_1-\Delta)^2-N/D_m^2$$

Δ is then the atomic weight term as represented in the later papers of Hicks, and is equivalent to the $2W$ of the first paper In triplet series the two separations give Δ_1 and Δ_2, of which the former is the greater

Hicks was led to conclude that there is a universal constant, approximately 0 21520, so that the denominator of the principal sequences of the alkalies, or of the sharp sequences in the elements of the second and third groups might be represented by

$$m+1-W\left(1-\frac{1}{m}\right)+a\left(1-\frac{k}{m}\right)sv$$

where a and k are constants for all elements, not very different from $0\ 002740/(1-k)$ and 0 21520 respectively v is the atomic volume, and s is an integer special to each element as follows

Na	2	Mg	8	Zn	9	Al	8
K	2	Ca	7	Cd	8	Ga	8
Rb	2	Sr	6	Hg	6	In	6
Cs	2					Tl	5

If k be taken $=0\ 21520$, $a=0\ 003490$ W is to be taken as $\Delta/2$ for doublets, and as Δ_2 for triplets

In order to indicate the degree of approximation given by the general formula, the following comparison may be made with the values of the denominators calculated from the regular series formulæ

Element	Series	At vol	s	$\Delta/2$	Δ_2	True denominator	From general formula
K	π_1	44 60	2	0 001466		(1) 2 233969	2 244315
						(2) 3 265225	3 277078
Ca	s_1	25 5	7		0·001368	(1) 2 484198	2 488903
						(2) 3 522799	3 555250
Zn .	s_1	9 33	9		0·003475	(1) 2 227899	2 229991
						(2) 3 257479	3 259785

It will be seen that the correspondence is far from perfect, and after the exhaustive investigation made by Hicks it may be doubted whether it is really possible to deduce such a formula which shall be applicable to all elements. The atomic volume, given by atomic weight divided by density, as Hicks remarks, varies with temperature and cannot be directly involved in the spectral relations, it would seem, however, that it may be closely related to an atomic property analogous to volume, or sphere of action, on which the structure of the spectrum in part depends.

It should be particularly noted that the atomic volume term, according to Hicks, does not appear in connection with the diffuse and fundamental series, in the alkalies it is associated with the principal sequence, and in other groups of elements with the sharp sequence.

The Oun.

Reference has already been made (p 46) to the discussion by Ritz of the terms $(p_1-p_2)/W^2$, from which it appeared that the range of values was much less for all elements than in the case of $\Delta\nu/W^2$ Hicks (III) has made a somewhat similar investigation, but has taken the whole denominator terms into account in forming the ratios Taking W as the atomic weight of an element, $w=W/100$, Δ the denominator difference which gives rise to the doublet separations, Δ_1 and Δ_2 the corresponding numbers for triplets, Hicks concludes that Δ is in all cases a multiple of qw^2, where q has the same value for all elements (=about 90 5, when Δ is multiplied by 10^6) The quantity qw^2 is that which Hicks has named the *oun* ($\omega\nu$), each element thus having an oun peculiar to itself and dependent upon the atomic weight The oun is designated δ_1, but the multiple $4\delta_1$ occurs most frequently and is indicated by δ We thus have

$$\delta_1=qw^2=1 \text{ oun for element of atomic weight } 100w$$
$$\delta=4qw^2=4 \text{ ouns}$$
$$10^6\Delta=m\delta_1 \text{ or } m\delta, \text{ where } m \text{ is an integer special to each element}$$

The derivation of the calcium oun may be taken for illustration The triplet separations are 105 89 and 52 09 The limits of the sharp series are 33983 45, 34089 34, and 34141 43, and when these are put in the form N/D^2, the denominators (D) are 1 796470, 1 793679, 1 792310 The denominator differences are therefore $\Delta_1=0\ 002791$, $\Delta_2=0\ 001369$, which are multiplied by 10^6 and tabulated as 2,791 and 1,369 The atomic weight is taken to be 40 124, so that $10^6\Delta_1/w^2=17336\ 1=48\times 361\ 169$, where the last factor is the number nearest to $4q$ which makes the multiplier an integer The value of δ for calcium is thus $361\ 169\times(0\ 40124)^2=58\ 14$, or $\delta=10^6\Delta_1/48=58\ 14$

This process has been applied by Hicks to a large number of series, and some of the results are given in the following table

	$\sigma_1\infty$	$W=100w$	$\Delta\nu$ (Sepn)	$10^6\Delta$	$10^6\Delta/w^2$	mq or $m\ 4q$	$\delta=4qw^2$ =4 ouns	361 8 ±
Na	24475 40	22 998	17 175	743	14027 96	155× 90 50	19 17	0 2, 0 14
K	21964 44	39 097	57 87	2,939	19224 86	53×362 72	55 45	0 92, 3 22
Rb	20871 29	85 448	237 54	12,935	17715 86	49×361 40	203 77	−0 40, 0 56
Cs	19673 00	132 823	553 80	32,551	18449 48	51×361·74	638 22	−0 06, 0 33

The last column gives the difference between 361 8 and the number under $4q$, except that when it is not the $4\times 90{\cdot}5$ term it is brought up to it by multiplying by 4. The second set of figures in this column shows the limits of permissible variation of the deduced $4q$, due to uncertainties in the measures of the lines In nearly all cases the differences from 361 8 are within the possible errors depending upon imperfect data

In this way, Hicks found from 17 elements, weighted according to the possible errors.

$$1 \text{ oun}=\delta_1=(90\ 4725\pm 0\ 013)w^2$$
$$4 \text{ ouns}=\delta=361\ 89w^2$$

The oun, according to Hicks, appears in connection with series in several other ways. The satellite separations, for example, are dependent upon multiples of the oun, and in the case of triplets $\Delta_1-2\Delta_2$ is also an oun multiple

It should be observed that formulae for series do not enter into this discussion, except as regards the adopted value of N and the determination of limits Except when the oun is very small, Hicks believes that with the accuracy now attainable in spectroscopic observations, it should be possible to obtain far more reliable values of the ouns of the various elements, and thence of the atomic weights, than by processes depending upon weighing There is, however, usually no apparent regularity in the multiplying integers which determine the doublet or triplet separations, even among elements of the same group, so that the simplest application of the spectroscopic method is to assume an approximate atomic weight in order to evaluate the multiple, and then to use this to correct the atomic weight

By this method Hicks has since made determinations of the atomic weights of copper and gold, taking silver as standard with atomic weight 107 88 * The results may be summarised as follows —

	Doublet separation ($\Delta\nu$)	$\sigma_{1\infty}$	$10^6\Delta$	δ	Multiple of δ	$W=100\sqrt{\delta/4q}$
Cu	248 44	31523 48	7307 087	146 1419	50	63 5569 $\pm$ 006
Ag	920 438	30644 60	27786 57	421 047	66	107 88(assumed)
Au	3815 56	29469 85	113951 00	1406 802	81	197 193 $\pm$ 003

The value of the constant $4q$ deduced from Ag is 361 7837 $\pm$ 0038, and this was used in calculating the atomic weights of Cu and Au from the δ terms Brauner's values are 63 56 $\pm$ 01, 197 20 $\pm$ 07 respectively for these elements It should be observed that the separations of the pairs of lines involved in these determinations can be measured with great accuracy, but that the exact determination of the limits of the series is less certain

In some cases the spectroscopic determination may be made independently of any previous knowledge of the atomic weight, by utilising the various different ways in which the oun is considered to play a part in building up the spectrum, and finding the greatest common factor An illustration is given later (p 58)

Collaterals

Further evidence of the oun as a controlling influence on the spectrum is adduced by Hicks from the supposed existence of what he has called " collaterals " In the case of doublets and triplets, the second, or second and third components may be considered as having received a sort of lateral displacement by the atomic weight term Δ, or Δ_1 and Δ_2, and may thus be regarded as collaterals of the first Hicks believes that this kind of displacement is not restricted to doublets and triplets, or their satellites, but is of very common occurrence Thus, if the wave-number of a series line be $N/D_1^2-N/D_m^2$, lateral displacements may be produced by the addition or subtraction of multiples of δ or Δ, say $x\delta$ or $x\Delta$, to D_1 or D_m When added to D_1 the operation is indicated by writing $x\delta$ to the left of the symbol of the original line, and when added to D_m to the right As an illustration, Hicks takes the Ca line at λ 6439 36 This may be represented by $(2\Delta_1+10\Delta_2)$ Ca $s_1(2)(+\Delta_2)$, meaning that whereas

$$\text{Wave No of Ca } s_1(2)=\frac{N}{(1\ 796470)^2}-\frac{N}{(2\ 484994)^2}$$

* Phil Mag, 38, 6 & 301 ; 39, 457

$$\text{Wave No. of Ca } 6439\ 36 = \frac{N}{(1\ 796470+2\Delta_1+10\Delta_2)^2} - \frac{N}{(2\ 484994+\Delta_2)^2}$$

$$= \frac{N}{(1\ 815732)^2} - \frac{N}{(2\ 486362)^2}$$

$$(10^6)\Delta_1 = 2791\,, \quad (10^6)\Delta_2 = 1369$$

In this way Hicks accounts for irregularities in the satellite separations which sometimes occur, and for discrepancies between the observed positions of certain lines and the positions calculated from formulae In some cases he considers that the whole set of lines for a given order number m may be replaced by another strong set displaced by several multiples of Δ, or by a congeries of fainter lines displaced by various oun multiples

The whole procedure, however, seems to be somewhat arbitrary, and it remains to be seen how it will bear the test when observations of sufficient accuracy for such a purpose become available Some of the examples first mentioned by Hicks are certainly no longer admissible, Mg $d_1(4)$, for instance (III, 356), has since been shown to be perfectly normal by the resolution of the line into two components *

Constitution of Diffuse Series

Hicks has further concluded that the diffuse and fundamental series cannot be represented by a continuous mathematical expression, though they may approximate to values so represented He considers it more probable that they depend on discrete changes which are connected with the oun, or atomic weight term, in a way which has yet to be discovered Thus, successive denominators (D) of a diffuse sequence are thought to differ by integral multiples of the oun When there are no satellites, the denominators change by multiples of Δ in the case of doublets, and of Δ_2 in the case of triplets, except that in the oxygen group the multiples are of Δ_1 When satellites are present, the multiples are of δ or δ_1 In addition, the decimal part, or mantissa, of the denominator of the normal first line of the diffuse series is itself a multiple of Δ, the outer satellite being taken as the normal line The general character of this part of the investigation will be sufficiently indicated by the first chief line and satellite of the diffuse series of caesium —

Cs $(10^6)\Delta = 32551$, $(10^6)\delta = 638\ 22$, $D_\infty = 19673\ 0$

Chief line		Satellite
$2\ 554329(228) - 76\xi - 43$	$46\delta_1$	$2\ 516989(226) - 97$
30δ		
$3\ 535183(200) - 201\xi + 40$	$51\delta_1$	$3\ 526567(200) + 9$
$10\delta_1$		
$4\ 533588(160) - 424\xi + 1$	14δ	$4\ 524635 - 161$
$3\delta_1$		
$5\ 533110(400) - 768\xi + 22$	14δ	$5\ 524175 - 26$
&c		

$$516989 = 857(638\ 260 \pm 0\ 233 - 0\ 0887\xi) = 857\delta$$

In this table the denominator terms have been adjusted within permissible limits indicated by the possible errors of observation The number in brackets following the denominator term is the estimated limit of error in the last three digits, ξ is the error of the limit, and the last number represents the difference

* Fowler & Reynolds, Proc Roy Soc, A **89**, 139 (1913)

between the observed value of the denominator and the "selected" value entered in the table The multiples of δ or δ_1 in the middle of the table are the satellite separations, expressed in terms of denominator differences

It is extremely difficult to form a just estimate of the confidence which may be placed in these results, on account of uncertainties in many of the observational data, and the occasional exceptions to the more general rules above stated Thus Cs is exceptional inasmuch as the first mantissa is a multiple of δ and not of Δ, and Cd is irregular because it is the mantissa of the chief line, and not that of the outer satellite, which is a multiple of Δ Very few spectra have been measured with the accuracy and completeness which would seem to be necessary to justify the deductions fully, and the adjustment of data within estimated permissible ranges is not an entirely satisfactory substitute The apparent absence of any general law governing the sequence of multiplying integers in the successive denominator terms is somewhat disappointing, for it is clear that the oun theory does not yet provide a guide to the identification of series lines such as is provided even by an approximate formula

Links.

In his fourth paper, Hicks has extended the idea of collateral displacements with a view to associating the lines which do not fall into the ordinary series with those which belong to the regular series systems Each line of a series is regarded as being connected with other lines in the same spectrum through several constant differences of wave-number, or *links*, which may be added or subtracted to an indefinite extent, and apparently in any order The various links which occur in a doublet system are distinguished by letters which have the following meanings as given by Hicks, and as written in the more extended notation of this report —

$$
\begin{array}{ll}
a=p-p(\Delta) & =N/(1+p_1)^2-N/(1+p_1+\Delta)^2 \\
b=p(-\Delta)-p & =N/(1+p_1-\Delta)^2-N/(1+p_1)^2 \\
c=p(-2\Delta)-p(-\Delta) & =N/(1+p_1-2\Delta)^2-N/(1+p_1-\Delta)^2 \\
d=p(-3\Delta)-p(-2\Delta) & =N/(1+p_1-3\Delta)^2-N/(1+p_1-2\Delta)^2 \\
e=p(-3\Delta)-p(\Delta) & =N/(1+p_1-3\Delta)^2-N/(1+p_1+\Delta)^2 \\
u=s-s(\Delta) & =N/(1+s)^2-N/(1+s+\Delta)^2 \\
v=s(-\Delta)-s & =N/(1+s-\Delta)^2-N/(1+s)^2
\end{array}
$$

As before, Δ is the denominator difference corresponding with the normal doublet separation The link b is the normal doublet separation, and link $e=a+b+c+d$

These methods were first applied to the spark spectra of silver and gold, containing 600 and 741 lines respectively in the region covered by the investigation. It will suffice to take silver as an illustration —

Ag		Links	Corrections to links
$p=\sigma_1\infty$	$=30644\ 60$	$a=880\ 77$	$a'-a=-0\ 61x$
	$=N/(1\ 891807)^2$	$b=920\ 44$	$b'-b=-0\ 61x$
$s=\pi\infty$	$=61116\ 33$	$c=962\ 54$	$c'-c=-0\ 66x$
	$=N/(1\ 339600)^2$	$d=1007\ 26$	$d'-d=-0\ 71x$
$\Delta\nu$ (sepn)	$=\ 920\ 435$	$e=3771\ 00$	$e'-e=-2\ 59x$
$10^6\Delta$	$=27786\ 57$	$u=2158\ 64$	$u'-u=-2\ 25x$
$\delta=10^6\Delta/66$	$=\ 421\ 0087$	$v=2616\ 61$	$v'-v=-2\ 47x$

The links are, of course, in ordinary wave-number units

It is further suggested that the links may be varied by making them depend on

displacement operations on values of p and s which have already been displaced by small multiples (x) of δ or δ_1, thus, $a'=p(x\delta)-p(x\delta+\Delta)$, $b'=p(x\delta-\Delta)-p(x\delta)$, and so on The calculated changes of the links are then as shown under $a'-a$, &c

It will be seen that in a complex spectrum, with seven links and these permissible variations in each of them, there is room for many accidental coincidences, but the discussion of probabilities has convinced Hicks that the existence of the links, in the main, cannot be due to chance

The following (IV., 366) are among the numerous suggested links occurring in silver, the differences in wave-numbers of the lines being enclosed in brackets, and decimal parts of the wave-numbers of the lines being omitted —

(1)	30514	(2460 39)	32974	(2460 84)	35435	(2461 00)	37896	(2457 26)	40353
(2)	17814	(3777 32)	21591	(3779 86)	25371	(3778 01)	29149	(3778 56)	32928
(3)	30959	(3776 44)	34735	(3777 47)	38513	(3773 79)	42286	(2618 00)	44904

Hicks attaches great importance to these long series of the same links, as proving the reality of variations in the links Thus, the differences in the second row are regarded as representing a modified link of about 3778 44 as compared with the calculated $e=3771\ 00$ The normal e link is thus changed to $e(-3\delta)$, that is, $[3771\ 00+(3\times 2\ 59)]$ with an outstanding error of 0 33 The link to another line, $P_1(1)$ at 30471 is $-2156\ 59$, which is equivalent to $u(\delta)+0\ 20$

Proceeding in this way, Hicks has drawn up extensive tables and maps which are intended to show that a great number of lines may be connected with ordinary series lines by links and chains, but most of them are too complex for reproduction As giving some indication of the nature of the results, however, the short linkage starting from Ag $\sigma_1(4)$, ($\lambda 3981\ 87$, $\nu=25106\ 89$) may be mentioned The following are the observed wave-numbers and intervals between the successive lines —

		$\Delta\nu$
$\sigma_1(4)$	25106	
		918 71
$\sigma_2(4)$	26025	
		3777 54
	29803	
		919 58
	30722	
		−2619 34
	28103	

It may be deduced from Hicks's table (IV , 394) that these intervals are identified with links and modified links, such that

$$\begin{aligned}28103&=25106\ 89+b+e(-2\delta)+b(2\delta)-v(-\delta)\\&=25106\ 89+920\ 44+(3771\ 00+5\ 18)+(920\ 44-1\ 22)\\&\qquad-(2616\ 61+2\ 47)\\&=28103\ 65\end{aligned}$$

The observed ν is 28103 33 so that a correction of only −0 32, or of $\Delta\lambda=+\ 025$, is required to make the sum of the links exact $\sigma_2(4)$ is not a good observation and the assumption of the normal separation from $\sigma_1(4)$ is therefore permissible

Some of the linkage systems which have been traced out in this manner are of great complexity, that starting from Ag $\pi_2(1)$, for example, involves more than 280 lines

To what extent such results represent reality is not as yet very clear. Since

the numerical values of the various links have been determined from series of arc lines, it would scarcely be expected that they would be applicable also to spark lines, which, in all known spectra of this class, form independent series if series are recognisable at all

Summation Series

An entirely novel idea has been introduced by Hicks in the suggestion that summation as well as difference series may occur in spectra (V 343) That is, if there be an ordinary series $A-\varphi(m)$, there may also be a series $A+\varphi(m)$ In such cases the mean of two corresponding wave-numbers would obviously give the limit of the series very exactly

Series believed to be of this type were first noted by Hicks in association with supposed fundamental series of the rare gases, and others were afterwards suggested in connection with series of other types * In general, the limits of the *P*, *S*, and *D* series are far larger than $F\infty$, so that associated summation series would most frequently lie beyond the range of observation Hicks considers that the existence of summation series is fully established by his investigations, but the evidence so far put forward is far from convincing It is frequently necessary to introduce hypothetical displacements of unobserved lines which are out of range, and there is no apparent regularity in the intensities of the lines in the same set It would, therefore, not be possible to recognise any of the suggested summation series as such by ordinary inspection of photographs, or by any independent procedure Moreover, it is remarkable that none of the well-established series having limits less than say, wave-number 26,000 are repeated in inverse order in the ordinary range of observations in the ultra-violet

Independent Determination of Atomic Weight

As a further example of the possible use of the oun, the determination of the atomic weight of an element, without assuming any knowledge from chemical, operations, may be mentioned The procedure may be illustrated by the spectrum of zinc,† for which (10⁶) $\Delta_1=7201$, and (10⁶) $\Delta_2=3486$

We have $\Delta_1-2\Delta_2=232$, which may be a small multiple of δ_1, especially as Δ_1 and Δ_2 are nearly exact multiples of 232

The satellites to $D(2)$ give denominator differences of 581 and 348, the difference is again nearly 232, but this cannot be the oun because 581 and 348 are not multiples of 232 The satellites to $D(3)$ give denominator differences of 504 and 388, which differ by 116, or half of 232 But 116 cannot be the oun because, although it divides 581 and 348, it does not divide 504 and 388 The half of 116 fails to satisfy the imposed conditions, but one-third of 116, or 38 7, divides all the numbers given above No smaller number than this is required in any connection, and 38 7 is therefore the small oun of zinc, δ_1

Δ_1 should be an exact multiple of δ_1, in this case 186 δ_1, and so a more correct value of δ_1 is given by $7204/186=38\ 731$, or $\delta=154\ 92$

The atomic weight is then $\sqrt{(154\ 92\times100^2)-361\ 89}=65\ 43$

The example is merely by way of illustration, since the "adjusted" figures given by Hicks (III, 346) have been used As already remarked, it would be simpler to assume the chemical determination of the atomic weight, and to use the spectroscopic data merely as a means of correcting the assumed value

* Phil Mag, **38**, 6, and 301 (1919), **39**, 457 (1920)

† The author is indebted to Prof Hicks for this example

CHAPTER IX.

APPLICATIONS OF BOHR'S THEORY

It is not the purpose of the present Report to present an account of theories of the origin of spectra, but Bohr's theory* calls for some mention because of the simplified view which it gives of the structure of the spectra themselves

Our first idea as to the origin of spectral lines might very well have been that a line is produced by the revolution of an electron about a centre, and that the frequency of the line would correspond with the frequency of revolution in the orbit The analysis of spectra, however, has shown that the frequency of a line always appears as the difference of two "terms," neither of which represents a spectral line, though one may represent the limit of a series Hence, a complete theory must in the first place give a physical meaning to these terms, and in the second place explain how an emitted frequency comes to be the difference of two of them

Bohr adopts the "nucleus atom" theory of Rutherford, which supposes an atom to consist of a positively charged nucleus and a system of external electrons such that in the neutral atom the total negative charge of the electrons is equal to the positive charge of the nucleus † On this basis, with the aid of the quantum theory of radiation, Bohr has developed a theory of spectra which leads to formulæ for the spectra of hydrogen and ionised helium, and represents these spectra quantitatively The theory also gives a general indication of the structure of other spectra, but the difficulties involved in their calculation have not yet been overcome

A summary of the theory has already been given by Jeans in his report on "Radiation and the Quantum Theory,"‡ and later developments have been reviewed by Silberstein in a report on "The Quantum Theory of Spectra"§ Important extensions of the theory to the explanation of the "fine structure" of the lines of hydrogen and ionised helium have been made by Sommerfeld ‖

The Spectrum of Hydrogen

In the case of hydrogen, the atom consists of a nucleus having unit + charge, and a single electron in orbital motion around it The circumstances of this motion may be calculated from the ordinary laws of mechanics, but the electron is supposed only to be free to traverse certain specified orbits, which are determined in the case of circular orbits by the condition that the angular momentum is an integral multiple of $h/2\pi$, where h is Planck's constant of action When the electron moves in one of these "stationary" orbits there is no radiation, and emission occurs only when the electron passes from one stationary orbit to another Without attempting to indicate the mechanism of the passage from orbit to orbit, Bohr supposes that the transition is followed by the emission of a homogeneous radiation, the frequency of

* Phil Mag, **26**, 1,476 (1913) Dan Acad Sc, IV, 1, Parts I & II, pp 1-100 (1918)

† The nucleus itself is probably of complex structure, including hydrogen nuclei and electrons, and its effective charge is the "residual" charge, corresponding to the atomic number of the element —Rutherford, Proc Roy Soc, A **97**, 374 (1920)

‡ Phys Soc (1914)

§ London Adam Hilger (1920)

‖ Atombau und Spektrallinien, 2nd edition, p 306 (Braunschweig, 1921)

which can be determined from the quantum theory The energy radiated is equal to the difference of the energies of the electron in the two orbits concerned, and is assumed to be one quantum of magnitude $\epsilon=hn$, where n is the frequency At any instant, a single atom contributes to only one line of the spectrum, and it is the summation of the radiations from a large number of atoms that accounts for the whole series of lines

Taking E and M as the charge and mass of the nucleus, e and m as the charge and mass of the electron, the theoretical formula for the hydrogen spectrum, in a first approximation, is

$$\nu=\frac{2\pi^2E^2e^2}{ch^3}\quad m\left(\frac{1}{\tau_1^2}-\frac{1}{\tau_2^2}\right)$$

where τ_1 and τ_2 are integers, c is the velocity of light, and $\nu(=n/c)$ gives the wave-numbers of the lines

When the mass of the electron is not considered negligible in comparison with that of the nucleus, and since $E=e$ in the case of hydrogen, the formula becomes

$$\nu=\frac{2\pi^2e^4}{ch^3}\quad\frac{Mm}{M+m}\left(\frac{1}{\tau_1^2}-\frac{1}{\tau_2^2}\right)$$

The formula is thus of precisely the same form as that which has been found to represent the spectrum of hydrogen (p 14), the expression outside the bracket representing the Rydberg constant The correspondence is not merely qualitative, as would be expected from the assumptions which have been made, but the theoretical agrees with the observed value within the limits of experimental errors *

When $\tau_1=2$ and $\tau_2=3$, 4, 5 the formula represents the Balmer series, if $\tau_1=1$, $\tau_2=2$, 3 we get the far ultra-violet series observed by Lyman, and if $\tau_1=3$ we get the infra-red series partially observed by Paschen

The radii of the stationary orbits vary as the squares of the integers τ, the theoretical values being given by

$$a=\frac{\tau^2h^2}{4\pi^2e^2m}$$

The successive orbits may thus be represented as in Fig 9 by drawing circles with radii 1^2, 2^2, 3^2 In the normal state of the atom, the electron revolves in the innermost orbit When the atom is disturbed, as by the electric discharge in a vacuum tube, so that the electron is removed to a great distance from the nucleus, the electron will generally occupy successively different orbits on its return The first line of Lyman's ultra-violet series corresponds to the fall of the electron from orbit 2 to orbit 1, the second line to the fall from orbit 3 to orbit 1, and so on. Similarly, the lines of the Balmer series are produced by falls from orbits 3, 4, 5 . . to orbit 2, and the lines of the infra-red series by falls from orbits 4, 5 to orbit 3

* Using Millikan's data (" The Electron," p 210), $e=4\,774\times10^{-10}$, $h=6\,545\times10^{-27}$, $e/m=1\,767\times10^7$, the theoretical value of N, in terms of oscillation frequency, is $3\,294\times10^{15}$, as compared with the spectroscopic value $3\,290\times10^{15}$ The substitution is conveniently made in the equation

$$N=\frac{2\pi^2e^5}{h^3e/m}$$

On this view, the line spectrum of hydrogen should include no lines other than those represented by the general formula

$$\nu = N\left(\frac{1}{\tau_1^2} - \frac{1}{\tau_2^2}\right)$$

There is no place for any of the lines observed in stars by Pickering, or calculated by Rydberg, which were formerly attributed to hydrogen This conclusion, it may be stated at once, is in complete accordance with our present experimental evidence

The series of lines discovered by Pickering in the star ζ Puppis appeared to converge to the same limit as the Balmer series of hydrogen, and to be closely represented by substituting $(\tau_2 + 0\,5)$ for τ_2 in the Balmer formula This relation would be appropriate to the diffuse and sharp series of the same element, and thus

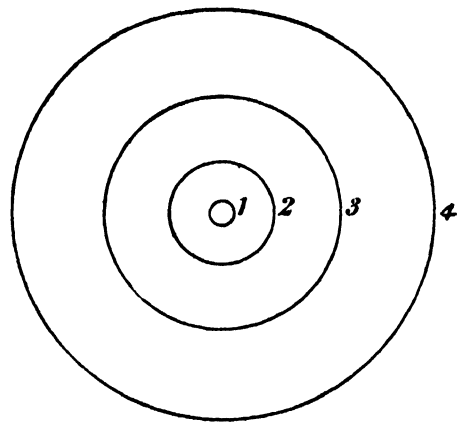


FIG 9 —THE BOHR ORBITS FOR HYDROGEN.

suggested that the Pickering lines were due to a form of hydrogen which could not be produced in the laboratory, but might be supposed to exist in stars at very high temperatures Adopting this view, Rydberg calculated the lines of the associated principal series, in accordance with the relations found for other elements, from the formula

$$\nu = N\left(\frac{1}{1\,5^2} - \frac{1}{\tau_2^2}\right)$$

The first " principal " line, given by $\tau_2 = 2$, would thus be at λ4,688, the second at λ2,734, and so on. All but the first lie beyond the region of atmospheric transparency, but the actual occurrence of a prominent line near 4,688 in ζ Puppis, as well as in many Wolf-Rayet stars and gaseous nebulæ, seemed to give strong support to Rydberg's theory, and the existence of a modified form of hydrogen was widely accepted Lockyer designated it " proto-hydrogen," in the belief that it represented one of the final stages of simplification of matter by the action of high temperatures ; it was also sometimes called " cosmic hydrogen "

Lines corresponding closely with this hypothetical spectrum were eventually obtained by Fowler* in experiments on helium in which hydrogen was present as

* Monthly Notices R A S , 73, 62 (1912). Phil Trans , A 214, 254 (1914).

an impurity The wave-length of the supposed first principal line as determined in the laboratory was slightly lower than that calculated by Rydberg, viz , 4,685 98 on Rowland's scale, but was at first supposed to be in sufficient agreement In addition to the lines 4,688, 2,734, &c , predicted by Rydberg, however, an intermediate series was found, with lines at λ3,203, &c , which was provisionally regarded as a second principal series, since its limit was identical with that of the " 4,686 " series Three of the Pickering lines were also produced, their wave-lengths being approximately 5,411, 4,541, 4,200 In accordance with Rydberg's theory, these also were at first attributed to hydrogen, for they seemed to have a close numerical connection with the Balmer series, and no relation whatever to the known lines of helium

The view that the lines in question were due to hydrogen, however, was not entirely satisfactory, partly because they could not be produced from hydrogen alone, and partly because the occurrence of lines not predicted by Rydberg broke the analogy with the series of other elements Fowler sought to estimate the value of the numerical evidence on which the identification with hydrogen mainly depended by a search for other examples of series of the " second principal " type, but the whole question was satisfactorily settled by Bohr in the extension of his theory to ionised helium

Ionised Helium (He^+).

There is good reason to believe that the helium atom consists of a doubly-charged nucleus of four times the mass of the hydrogen nucleus, with two electrons revolving round it When the gas is subjected to discharges of moderate intensity, one of the electrons may be supposed to be displaced, and the ordinary spectrum of helium to be emitted when this moves to different orbits on its return , the theory of this spectrum, however, is not yet complete Under the action of sufficiently strong excitation, both electrons are supposed to be removed from the normal orbit, and a second totally different spectrum to be emitted when only one of them returns The formula for the series of lines developed will be identical in a first approximation with that for hydrogen, except that E is now to be replaced by $2e$, thus

$$\nu=\frac{8\pi^2e^4m}{ch^3}\left(\frac{1}{\tau_1^2}-\frac{1}{\tau_2^2}\right)=4N\left(\frac{1}{\tau_1^2}-\frac{1}{\tau_2^2}\right)$$

When the mass of the electron is taken into account

$$\nu=\frac{8\pi^2e^4}{ch^3}\,\frac{M'm}{M'+m}\left(\frac{1}{\tau_1^2}-\frac{1}{\tau_2^2}\right)=4N'\left(\frac{1}{\tau_1^2}-\frac{1}{\tau_2^2}\right)$$

where $M'=4M$, and N' differs slightly from N

When τ_1 is put $=3$ in the approximate formula, the substitution of 4, 6, 8 for τ_2 will obviously give lines identical in position with those calculated for the supposed principal series of hydrogen by Rydberg, while $\tau_2=5$, 7, 9, will give lines nearly coincident with the " second principal " series of hydrogen observed by Fowler Bohr's theory, however, unites both in a single series of a new type, and assigns them to ionised helium The small deviations of the observed lines from Rydberg's calculated values are accurately accounted for by the difference between N and N', depending upon the difference of atomic weights

As to the Pickering lines, Bohr's theory indicated that associated with these in a single series there ought to be lines nearly coincident with the Balmer series of

hydrogen, the Pickering lines being given by $\tau_1=4, \tau_2=7, 9, 11$, and the additional lines by $\tau_2=6, 8, 10$. The observation of some of the additional lines by Evans* and subsequently by Paschen,† together with the observations of the lines in the absence of all traces of hydrogen, gave additional support to the theory which attributes them to ionised helium

The Pickering series, as thus extended, is compared with the Balmer series in Fig 10 The difference in position of the lines at H_α is 2 6*A*, diminishing to 1 6*A* at H_ϵ Expressed numerically, the formulæ for H and He^+ are respectively

$$\nu=109678\ 3\left(\frac{1}{\tau_1^2}-\frac{1}{\tau_2^2}\right)$$

$$\nu=(4\times109723\ 22)\left(\frac{1}{\tau_1^2}-\frac{1}{\tau_2^2}\right).$$

The ratio $\frac{N_{He^+}}{N_H}$ as thus determined from Fowler's observations is 4 001638.

The theoretical ratio is $\frac{4M_{He}(M_H+m)}{M_H(M_{He}+m)}$, and taking $M_H/m=1845$ in accordance with Millikan's experimental result, the numerical value is 4 001626, in close accordance with the observed ratio

Conversely, the observed ratio may be utilised to derive the mass of the electron in terms of that of the hydrogen nucleus, giving $M_H/m=1831$ ‡

Paschen§ has made a further investigation of the spectral constants, with relativity corrections and other refinements, and has obtained $M_H/m=1843\ 7$.

There is now ample evidence both theoretical and experimental, that Rydberg's

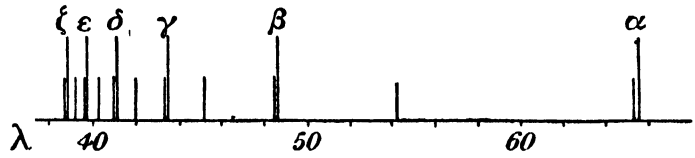


FIG. 10 —COMPARISON OF EXTENDED PICKERING SERIES WITH BALMER SERIES OF HYDROGEN

hypothetical lines of hydrogen have no existence, and that the lines observed in stars and in the laboratory near their positions are really the enhanced lines due to ionised helium Further support for this conclusion is afforded by Fowler's demonstration that enhanced lines of other elements also have 4*N* for the series constant

It will be observed that on Bohr's theory the Balmer and associated series represent the final simplification of the hydrogen spectrum, and that the " 4686 " and associated series similarly represent the simplest possible spectrum of helium In other elements, however, it is conceivable that further simplifications may occur, corresponding to the loss of two or more electrons and giving rise to series having 9*N*, or still higher multiples, for the series constant. The existence of such series

*Phil Mag, 29, 284 (1915)
†Ann d Phys, 50, 901 (1916)
‡Fowler's original value, when the measures were expressed on Rowland's scale, was 1836±12.
§ Loc cit

has not yet been completely demonstrated On account of the high value of the series constant, the strongest lines of this class will probably lie in the extreme ultra-violet

Arc Spectra.

The theory has not yet been developed so as to give a complete representation of the spectra of elements other than hydrogen and ionised helium In neutral helium, which is the next in order of simplicity of atomic structure, the ordinary spectrum arises from the interaction of a displaced electron with a system consisting of the nucleus and the other electron The residual charge of the central system is thus one unit, as in hydrogen, and the force on the electron, when at a great distance from the nucleus, will be nearly the same as in the hydrogen atom The series constant for the spectrum of the neutral atoms will therefore be nearly the same as that for hydrogen The detailed discussion of the possible stationary orbits indicated by the actual spectrum, however, is very complicated

A similar consideration of the spectra of elements in which the atoms include a larger number of electrons suggests an explanation of the appearance of the Rydberg constant in the formulae for series of other elements

The series constant may be expected to show a small variation with the atomic weight of the element, as already indicated in the case of helium Thus, if M be the mass of the atomic nucleus, and m that of the electron, the Rydberg constant for hydrogen is of the form

$$N_H = k\frac{Mm}{M+m}$$

For any other element of atomic weight A in terms of hydrogen,

$$N_A = k\frac{AMm}{AM+m}$$

and we have the ratio

$$\frac{N_A}{N_H} = \frac{A(M+m)}{AM+m} = \frac{M/m+1}{M/m+1/A}$$

Taking Millikan's value for hydrogen $M/m=1845$, we get

$$\frac{N_A}{N_H} = \frac{1846}{1845+1/A}$$

With Curtis's value 109678 3 for N_H, we thus find $N_{He}=109722\ 9$, $N_{Li}=109729\ 25$, and $N_\infty=109737\ 7$ *

It is only in connection with hydrogen and ionised helium, however, that the precise value of N is at present of importance With the approximate series formulae adapted to other spectra, the hydrogen constant may be used without disadvantage in ordinary calculations

Spark Spectra

The series of enhanced lines which are especially developed in spark spectra, as first clearly shown by Fowler† for Mg, Ca, and Sr, are characterised by the appearance of the series constant with four times its ordinary value. Such series,

* In a discussion of data relating to the fine structure of the lines, R T Birge has deduced the value 109677 7±0 2 for hydrogen, and 109736 9±0 2 for a nucleus with infinite mass Phys Rev , **17**, 589 (May, 1921)

† Bakerian Lecture Phil Trans , A **214**, 225 (1914)

as in ionised helium, are therefore to be attributed to the ionised elements; that is, two electrons are to be supposed removed by the exciting source, and the enhanced series to be produced when one of them returns, the central system then having a net charge of two units. When the second electron returns its interaction is with a central system having only one unit charge, and the ordinary arc series are developed, the atom as a whole is then neutral. The two spectra are as different as if they belonged to two different elements, and since the systems producing them cannot co-exist, there are no lines arising from combinations of the terms of the arc and spark series.

As a general conclusion from Bohr's theory, it would thus appear that all series having N for the series constant are produced by neutral atoms, while those having $4N$ for the constant have their origin in ionised atoms. If three electrons were removed by the exciting source, the return of one of them while two remained detached would be marked by the appearance of series having $9N$ for the series constant, and so on.

It should be observed that the energy necessary to produce the enhanced lines varies from element to element. In Ca, Sr, Ba, for example, these lines are strongly developed even in the ordinary arc, though they are relatively much strengthened in the spark (*see* Plate IV.). In many elements, including the alkali metals, on the other hand, such lines do not appear at all under the stimulus of the arc.

A possible connection between the limits of the principal series of enhanced lines and the limits of the principal series of singlets in the arc spectra of the elements of Group II. has been noted by E. Fues,* namely, that the former are about double the latter. He gives the following data in illustration —

	Mg	Ca	Sr	Zn	Cd
$P\infty$ (=1 5S)	61,660	49,300	45,900	75,760	72,540
$\pi\infty$ (=1 5σ)	121,270	95,700	88,850	159,000	151,000
$\frac{1\ 5S}{1\ 5\sigma}$	0 509	0 515	0 518	0 477	0 480

The ratios for Zn and Cd, with the limits shown in the tables which follow (147,544 and 140,226 respectively), are 0 514 and 0 517, in closer agreement with the remaining three values.

Graphical Representation of Series Systems

Since the wave numbers of the spectral lines always appear as differences of pairs of terms, the whole set of series and combinations may be very conveniently represented by plotting the "terms" which give rise to them. The various lines will then be represented by differences between the terms taken two by two. Such diagrams obviously have no necessary connection with any particular theory of spectra, but they are especially instructive when the terms are regarded as representing the stationary orbits of Bohr's theory.

Thus, for hydrogen, in place of drawing the orbits as in Fig. 9, it is convenient to plot the terms N/m^2 as in Fig. 11 (m being an integer), and to regard them as representing small portions of the successive orbits, although they are not to the true scale of radii. Following a suggestion made by Birge,† the logarithms of the terms have been plotted, and not the terms themselves, as this has the advantage of

* Ann. d. Phys. **63**, 19 (1920).

† In a paper by Foote and Meggers, Phil. Mag., **40**, 80 (1920).

opening out the higher terms as compared with the lower Regarding the lines as representing the non-radiating orbits, the nucleus is situated away to the right of the diagram, and the actual spectral lines correspond to the fall of electrons from orbits on the left to orbits on the right By this method the three series of lines which would be required to represent the known spectrum of hydrogen are reduced to a single series of term values

This simplification is of greater importance in connection with more complex spectra, as will appear from the examples given in Fig 12 In all cases the terms plotted are those of the sharp, principal, diffuse and fundamental series, and these are distinguished by making the lines of different lengths The two values for the terms of the principal series in doublets, or three terms in the case of triplets, are usually too close to be conveniently represented separately, and they have been indicated in the diagrams by breaking the corresponding lines into two or three equal portions, as the case may be Similarly, the fact that there are sometimes two or three values of the diffuse series terms, arising from the presence of satellites, has been indicated by appropriate breaks in the upper portions of the lines

The first diagram represents the orbit terms for the doublet system of sodium The falls from the π orbits to the innermost orbit, 1σ, give the principal series, consisting of pairs with diminishing separation The falls from the σ and δ orbits to

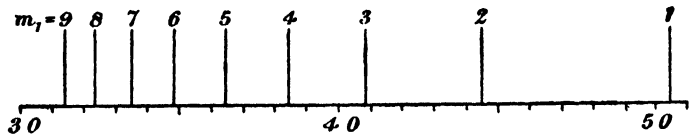


FIG 11 —TERMS OF THE HYDROGEN SPECTRUM (log N/m^2)

the two adjacent orbits represented by $1\pi_1$ and $1\pi_2$, yield the constant separation pairs of the sharp and diffuse series respectively, falls from the φ orbits to the orbit 2δ give the fundamental series consisting of single lines It will be seen that the various combinations can be considered in the same way The orbits shown in the sodium diagram are 51 in number, and the lines which are actually represented in the tables by the various combinations of these terms are 98

The second diagram represents in a similar manner the triplet system of magnesium Here there are two sets of orbits, one corresponding to the triplets and the other to the singlets There are no satellites In the triplet system, the $1p$ orbits lie inside the $1s$ orbit, but the innermost orbit is that represented by $1S$ Inter-combinations between the two sets of orbits have been found to exist, as will appear from the tables

The third diagram represents the doublet system of ionised magnesium, closely resembling the system of sodium The term 1δ is not certain, but analogy with calcium, strontium and barium suggests that it may exist Also, according to Fowler's analysis, the observed series of fundamental type (which includes λ4481) has its limit at 2δ, and the separations of its constituent lines are out of step with the fundamental series of the other alkaline earth elements The real fundamental series possibly has 1δ for limit, and its lines in the extreme ultra-violet, but the absence of the lines $1\delta - 1\pi_{1,2}$ which appear in the other elements of the group, throws doubt on this interpretation This diagram is of special interest in connection with the fact that while some of the enhanced lines of magnesium occur quite strongly

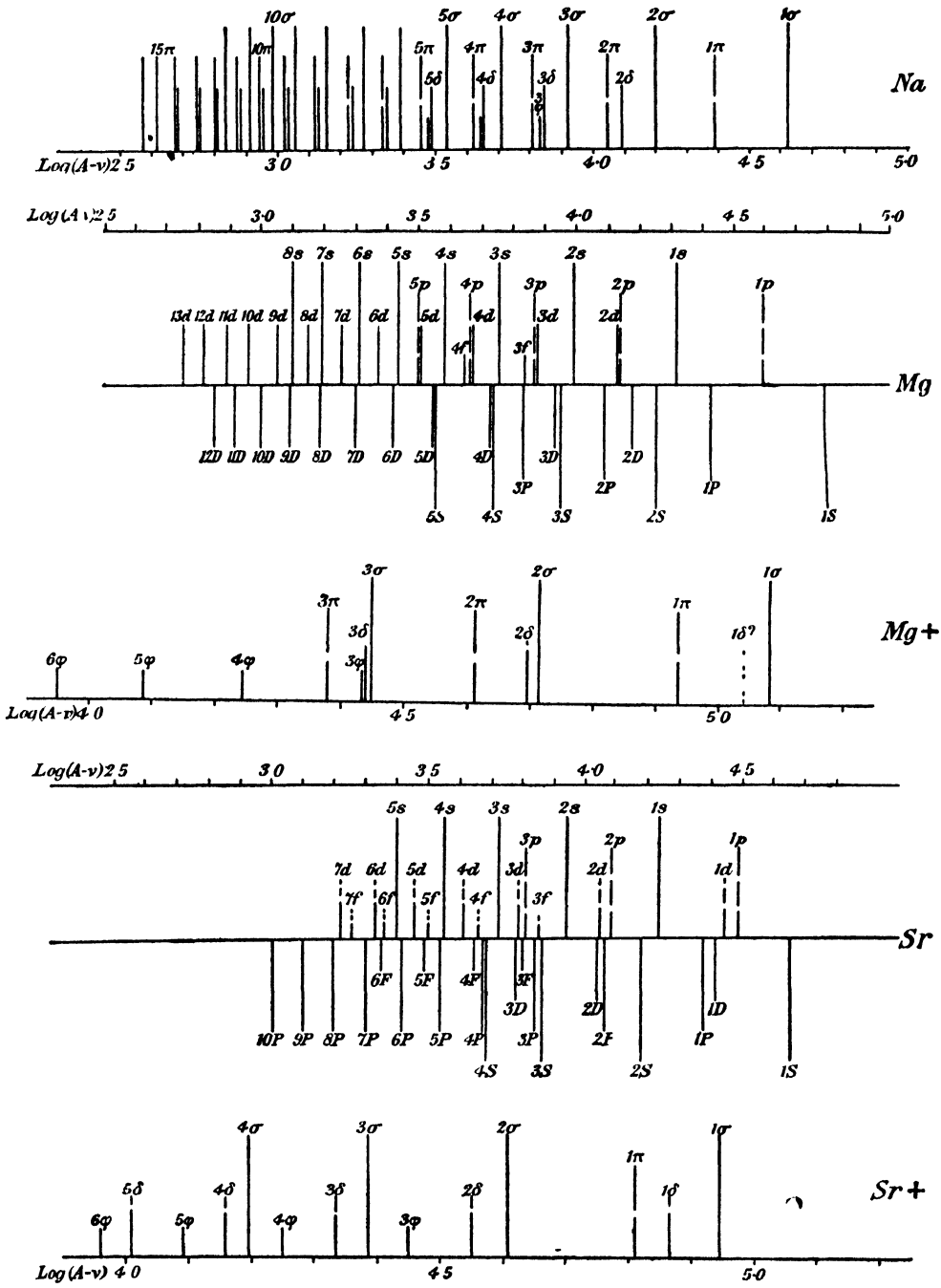


FIG 12.—TERMS OF THE SPECTRA OF Na, Mg, Mg+, Sr, Sr+

in the arc in air (*see* introduction to tables of magnesium series), there are others, belonging to the same series system, which only occur under spark conditions, or their equivalent in the arc *in vacuo* * It was previously somewhat difficult to understand why the line 4481 (2δ-3φ) did not appear simultaneously with lines like λ 2795, 2802 ($1\sigma-1\pi_{1,2}$) in the arc in air, since all the lines belong to series with $4N$ for constant. In the light of Bohr's theory, as illustrated by the diagram, it would appear that in the arc in air the second electron is not removed to an indefinitely great distance from the nucleus, but only to a distance which is something less than the radius of the orbit corresponding to the term 3φ Under these conditions, there could be no combinations involving 3φ or any of the terms to the left of 3φ in the diagram Under spark conditions, however, the stimulus is sufficient to remove two electrons to " infinity," so that the entire system of enhanced lines will be produced when one of the electrons returns The return of the second electron would, of course, render the atom neutral, and the arc series would be developed

The fourth diagram represents the triplet system of strontium, which is similar to that of magnesium, except that satellites are present in both the diffuse and fundamental series

The last of the diagrams, for ionised strontium, is similar to the corresponding diagram for magnesium, except that satellites occur in the diffuse terms, and that the term 1δ is certainly indicated by the observations Since there are two values for 1δ, falls from the φ orbits to 1δ will yield doublets in the fundamental series

In each case, of course, there may be other combinations of terms, or orbits, besides those which give rise to the four main series Some of the combinations, however, are more probable than others, and these probabilities have been embodied by Bohr† in the so-called " selection principle "

Ionisation Potentials and Spectral Series

Experiments on the ionisation potentials of gases and vapours have an important bearing on Bohr's theory and upon the interpretation of some of the changes of spectra under different experimental conditions In such experiments, the gas or vapour is bombarded by electrons from a glowing filament, and the electrons are accelerated by an adjustable electric field. The energy of the bombarding electrons is known from the potential difference through which they fall Thus, if the potential difference is indicated by V and the velocity of the electron by v,‡ we have

$$eV=\tfrac{1}{2}mv^2$$

In the case of hydrogen, Bohr's theory gives the negative energy corresponding to the different stationary orbits as

$$W_\tau=\frac{2\pi^2me^4}{\tau^2h^2}$$

where τ is the integer defining the orbit This is equal to the energy required to remove the electron to an infinite distance from the nucleus

* As a simple working hypothesis, it may be supposed that in air a large amount of energy is required to separate two electrons from the nucleus, while in the arc in vacuo a smaller amount of energy suffices on account of the greater freedom of movement of the electrons

† Zeit f Phys , 2, 423 (1920) *See* also Sommerfeld's book, p 387

‡ Since 1 volt $=10^8$ e m u $=1/300$ e s u , and $e/m=1\ 767\times10^7$ e m.u $=5\ 301\times10^{17}$ e s u , the velocity corresponding to 1 volt will be about $5\ 9\times10^7$ cm /sec

When the electron passes from one orbit to a smaller one, it is assumed that the difference of energies is radiated as a quantum, hn, of frequency n, thus

$$W_{\tau_1}-W_{\tau_2}=\frac{2\pi^2me^4}{h^4}\left(\frac{1}{\tau_1^2}-\frac{1}{\tau_2^2}\right)=hn$$

so that

$$n=\frac{2\pi^2me^4}{h^3}\left(\frac{1}{\tau_1^2}-\frac{1}{\tau_2^2}\right)$$

or, if ν be the corresponding wave-number, and c the velocity of light,

$$\nu=\frac{2\pi^2me^4}{ch^3}\left(\frac{1}{\tau_1^2}-\frac{1}{\tau_2^2}\right)=N\left(\frac{1}{\tau_1^2}-\frac{1}{\tau_2^2}\right)$$

which is the formula already quoted for hydrogen

We thus have

$$W_\tau=chN\frac{1}{\tau^2}$$

and

$$W_{\tau_1}-W_{\tau_2}=chN\cdot\left(\frac{1}{\tau_1^2}-\frac{1}{\tau_2^2}\right)$$

where N is the Rydberg constant (in wave-number)

For series spectra in general, using the Rydberg formula for simplicity, we shall have

$$W_{\tau_1}-W_{\tau_2}=chN\left[\frac{1}{(\tau_1+\mu_1)^2}-\frac{1}{(\tau_2+\mu_2)^2}\right]$$

For comparison with the results of ionisation experiments, the work necessary to remove the electron from one orbit to another is most conveniently expressed in terms of equivalent volts, by putting $W_{\tau_1}-W_{\tau_2}=eV$, where V is the potential difference through which the bombarding electron must fall to acquire the corresponding amount of energy We thus get the general expression

$$V=\frac{chN}{e}\left[\frac{1}{(\tau_1+\mu_1)^2}-\frac{1}{(\tau_2+\mu_2)^2}\right]$$

or (in volts)*

$$V=\frac{N}{8102}\left[\frac{1}{(\tau_1+\mu_1)^2}-\frac{1}{(\tau_2+\mu_2)^2}\right]$$

If ν be the wave-number of the spectral line which is produced by the return of the electron from orbit τ_2 to τ_1, we have finally

$$V=\frac{\nu}{8102}$$

Since the ionisation potential corresponds to the removal of an electron from the innermost orbit to infinity, τ_2 in this case $=\infty$, and the ionisation potential will be given by substituting for ν the limit of the series which extends furthest into the ultra-violet.

In the case of hydrogen, the innermost orbit is given by $\tau_1=1$, and $\nu=N/1^2$ $=109678\cdot3$ Hence, the theoretical value of the ionisation potential of hydrogen

$$\frac{ch}{e}=\frac{3\times10^{10}\times6\cdot545\times10^{-27}}{4\cdot774\times10^{-10}}\times300=\frac{1}{8102}$$

atoms is 13·5 volts The experimental determinations are of this order, but are complicated by the fact that energy is required to dissociate the molecules before the atoms can be ionised

The potential difference corresponding to the removal of an electron from the innermost orbit to the next one has been called the " resonance potential " or " radiation potential " The return of the electron to its normal position would then be followed by the emission of a single line, as observed by McLennan* and others in some elements In hydrogen the wave-number of the resonance line would be

$N\left(\frac{1}{1^2}-\frac{1}{2^2}\right)=82\ 258$, and the resonance potential 82,258/8102 = 10 1 volts

In the elements of Group I. the innermost orbit is that represented by the limit of the principal series, that is, by the term 1σ (=1 5 *s* of Ritz and Paschen) The second orbit is represented by the term $1\pi_1$ (2*p* of Ritz and Paschen), and the frequency of the resonance line is that of the first principal line, $1\sigma-1\pi_1$ (*see* Na, Fig 12) Hence, in Group I,

$$I\ P\ =\frac{1\sigma}{8102}\text{ volts}$$

$$R.P.=\frac{1\sigma-1\pi_1}{8102}\text{ volts}$$

Caesium, as observed by Foote and Meggers,† furnishes an interesting example Here we find $1\sigma=31{,}405$, and $1\sigma-1\pi_1=11{,}732$ The theoretical ionisation potential of caesium is therefore 3 876 volts, in remarkable accordance with the experimental value 3 9 volts Similarly, the calculated resonance potential is 1 448 volts, in close accordance with the observed 1 5 volts Similar results have also been obtained for sodium, potassium, zinc and cadmium ‡

In the triplet systems of Group II, which also include a singlet system (*see* Mg and Sr, Fig 12), the innermost orbit connected with the arc spectra is indicated by the limit 1*S* of the principal series of singlets, and we accordingly have

$$I\ P\ =\frac{1S}{8102}$$

The second orbit is represented by the term $1p_1$ of the triplet system, but the resonance line actually observed is the combination $1S-1p_2$ (=1 5*S*−2p_2 of Paschen). Thus, in this group

$$R\ P\ =\frac{1S-1p_2}{8102}$$

In mercury the resonance line $1S-1p_2$ is the well-known line in the ultra-violet, λ2,536, or ν39,410 The resonance potential of mercury is consequently 39,410/8102 = 4 9 volts A second resonance potential corresponds with the line $1S-1P$, $=\lambda$1,849 = ν54,066, its magnitude being 6 7 volts The term $1S$, = 84,177, is the highest in the system of arc series, and the ionisation potential of mercury is accor-

* Proc Roy Soc, **A. 92**, 305 (1916)
† Phil Mag, **40**, 80 (1920)
‡ Tate and Foote, Phil Mag, **36**, 64 (1918)

dingly 10 4 volts. These values are in close accordance with experimental determinations *

In calcium, two resonance potentials, and the ionisation potential, have been determined experimentally by Mohler, Foote and Stimson,† namely, 1 90, 2 85 and 6 01 volts. The corresponding theoretical values are

First resonance	$1S-1p_2=\lambda 6572\ 78=\nu 15210\ 3$,	$V=1\ 887$ volts.
Second ,,	$1S-1P=\lambda 4226\ 73=\nu 23652\ 4$,	$V=2\ 918$ volts.
Ionisation	$1S\quad=\lambda 2027\ 56=\nu 49304\ 8$,	$V=6\ 081$ volts

The calcium series are similar to those of strontium illustrated in Fig 12, and it will be observed that there is a preferential tendency for the electron to occupy orbits associated with principal series

Helium is of considerable interest in this connection Bohr's theory gives the total energy of the neutral helium atom as 6 13 times that of hydrogen,‡ so that the potential difference corresponding to the energy required to remove both electrons to infinity will be $6\ 13\times 13\ 5=82\ 7$ volts When the atom has already lost one electron, the energy necessary to remove the remaining electron is definitely given by the theory as four times that required for hydrogen, the equivalent in volts, therefore, being 54 0 This also follows from our formula, since the highest possible limit is $4N^1/1^2=438{,}892$, which, divided by 8,102, $=54\ 2$ volts For the first ionisation the theory accordingly gives the ionisation potential as $82\ 7-54\ 0=28\ 7$ volts It is not yet possible to predict the spectral lines of the neutral atom, but the theory thus points to $28\ 7\times 8{,}102$, $=\nu 232{,}530$, $=\lambda 430$ as the highest limit in the helium spectrum

Experiments appear to show that the first ionisation actually occurs at 25 5 volts, and the first radiation at about 20 volts § The innermost orbit would thus correspond to a series limit in the region of $25\ 5\times 8{,}102=\nu 206{,}600$, $=\lambda 484A$, and a resonance line would be expected at about $20\times 8{,}102=\nu 162{,}040$, $=\lambda 605A$ Experimental evidence of the probable existence of such frequencies in the spectrum of helium is furnished by the work of Richardson and Bazzoni‖ on the high-frequency limits of the spectrum of this gas The highest frequency thus determined was found to lie between $\lambda 470$ and $\lambda 420$, and probably nearer to the latter value, in general agreement with $\lambda 430$ for the limit of the series calculated from Bohr's theoretical value of the ionisation potential

Indirect evidence of the existence of lines in the far ultra-violet is also afforded by the fact that none of the known lines of helium appear as absorption lines until the gas is submitted to an electric discharge This is also the case with the Balmer series of hydrogen and suggests that the limit of the so-called principal series of helium does not represent the innermost, or normal, orbit In the alkali metals, the lines of the principal series are readily reversed at low temperatures, and the innermost orbits are represented by the limits of these series

* Franck and Hertz, Verh d D Phys Ges, **15**, 34 (1913) Davis and Goucher, Phys Rev, **10**, 84 (1917)

† Phil Mag, **40**, 73 (1920)

‡ Phil Mag, **26**, 489 (1913)

§ Horton and Davies Proc Roy Soc, A **95**, 408 (1919), Phil Mag, **39**, 592 (1920), Compton and Lilly, Astrophys Jour, **52**, 1 (1920)

‖ Phil Mag, **34**, 285 (1917)

The excitation of the enhanced lines of helium, corresponding to the second ionisation, has been found to require a potential difference of 80 volts, in good agreement with the theoretical value *

It will be gathered that a very important field of research has been opened up by these investigations of the connection between spectral series and the resonance and ionisation potentials They not only provide valuable tests of theories of the origin of spectra, but may help in the detection of series in spectra which have not yet been resolved In a doublet system (compare caesium, p. 70) the limit of the principal series, and the first line, could be calculated with fair approximation from the observed values of the ionisation and radiation potentials, and thence all the lines of the series, from the principal series, the sharp series could also be calculated approximately from the Rydberg relations Similarly, the principal series of singlets in a triplet system could be calculated from the ionisation potential and the second resonance potential, if it be established that the examples given above are typical.†

Spectral Series and the Periodic Table.

The analysis of spectra into their component series is not yet sufficiently complete to permit a full discussion of the relation between the spectra and the positions of the elements in the periodic classification, but there are several points of interest in this connection

In the first place, it is to be observed that all the elements of the same group give series of the same type, so far as they are known Omitting the inert gases, and referring first to the "arc" spectra yielded by neutral atoms, the elements of Group I present doublet systems, those of Group II triplets, and those of Group III doublets The remaining groups have not yet been completely sorted out into series In Group IV, probable series lines have only at present been identified in silicon, which gives triplets in the arc In Group V no series have yet been traced Oxygen, sulphur, and selenium of Group VI, however, give triplets

The interesting point is that doublets and triplets appear to alternate with each other through the first six groups Since the number of the group is supposed to indicate the valency (and also the number of electrons in the outer ring), it would seem that elements of even valency yield triplets, while those of odd valency give rise to doublets The only known exception is manganese, which gives triplets in the arc, whereas doublets would be expected according to the rule stated, the triplets, however, have not the same simplicity as those which occur in Group II, and there appears to be some doubt as to the number of electrons in the outer ring (Sommerfeld, p 304)

The elements of Group II, which give triplets in the arc, give series of enhanced doublets in the spark Those of Group III, so far as the series are known, give doublets in the arc, and evidence of the occurrence of triplets in the spark spectra of Al, Sc, Y, has been found by Popow. Elements of Group I, which give doublets in the arc, give spark spectra which have not been resolved into series, as in most of the inert gases

Thus, so far as these observations permit deductions, the spark spectrum of

* Rau Sitz Ber d Phys Med Ges zu Würzburg (1914), p 20, Compton and Lilly, loc cit

† Since the above was written, an important "Report on Photo-electricity, including Ionising and Radiating Potentials," by Prof A L Hughes, has been issued by the National Research Council, Washington (Bulletin, No. 10, 1921)

Periodic Classification of the Elements

	0	I	II	III	IV	V.	VI	VII	VIII
1 H 1 008									
	2 He 4 0	3 Li 7 0	4 Be 9 1	5 B 10 9	6 C 12 0	7 N 14 01	8 O 16 00	9 F 19 0	
	10 Ne 20 2	11 Na 23 00	12 Mg 24 32	13 Al 27 1	14 Si 28 3	15 P 31 0	16 S 32 07	17 Cl 35 46	
	18 A 39 9	19 K 39 10 29 Cu 63 56	20 Ca 40 1 30 Zn 65 38	21 Sc 44 1 31 Ga 69 9	22 Ti 48 1 32 Ge 72 5	23 V 51 2 33 As 74 96	24 Cr 52 0 34 Se 79 2	25 Mn 54 9 35 Br 79 9	26 Fe 27 Co 28 Ni 55 8 58 97 58 68
	36 Kr 82 9	37 Rb 85 45 47 Ag 107 88	38 Sr 87 63 48 Cd 112 4	39 Y 88 8 49 In 114 8	40 Zr 90 6 50 Sn 119 0	41 Nb 93 2 51 Sb 120 2	42 Mo 96 0 52 Te 127 5	43 53 I 126 9	44 Ru 45 Rh 46 Pd 101 7 102 9 106 7
	54 Xe 130 2	55 Cs 132 8 79 Au 197 2	56 Ba 137 37 80 Hg 200 4	57–71 Rare Earths 81 Tl 204 0	72 82 Pb 207 1	73 Ta 181 2 83 Bi 208 0	74 W 184 0 84 Po	75 85	76 Os 77 Ir 78 Pt 190 9 193 1 195 2
	86 Nt (Em) 222 4	87.	88 Ra 226 4	89 Ac 226	90 Th 232 2	91 UX_2 234	92 U 238 2		
Neutral atoms R Ionised atoms R+ Second ionisation R++ Third ionisation R+++		*d* *d*	*t* *t* *d* *d*	*d* *t*?	*t*(Si) *d*(C, Si) *t*?(C, Si) *d*?(C, Si)	*d*?(N)	*t* *d*?(O)	*t*(Mn) *t*?(F,Cl)	*d*=doublets *t*=triplets

an element has the same character as the arc spectrum of the element adjacent to it in the preceding group of the periodic table This relation is explicable on the supposition that the loss of an electron from the outer ring reduces the valency of the element by 1 and so displaces it to the preceding group Attention was first directed to this relation by Kossel and Sommerfeld,* who have called it the *displacement law*, from analogy with the displacement law in radio-activity

Further evidence in support of this "law" is given by certain unpublished observations made by the author In Group IV , definite series of enhanced doublets, with $4N$ for constant, have been identified in carbon and silicon There is evidence also of a "second-step" ionisation in each of these elements (C^{++} and Si^{++}) giving triplets and possibly representing a displacement of two places to the left in the table , and of a "third-step" ionisation (C^{+++} and Si^{+++}) represented by a system of doublets and corresponding to a possible displacement of three places to the left A final test of these suggestions requires the extension of the observations into the far ultra-violet so as to permit calculations of the series constants, which should be $9N$ and $16N$ respectively. In Group V there are doublets among the spark lines of nitrogen which possibly represent the second-step ionisation, N^{++} In Group VI the second, or spark, spectrum of oxygen shows several doublets which perhaps represent O^{+}. In Group VII fluorine and chlorine show triplets under spark conditions, which, however, have not yet been arranged in series

These observations are summarised in the accompanying table of the elements, in which it is to be understood that *d* ? and *t* ? indicate that the evidence is not complete

On theoretical grounds Kossel and Sommerfeld also suggested a possible numerical relation between the spark spectrum of an element and the arc spectrum of the element which precedes it in the periodic table Since the doublet separation in the subordinate series is determined by the difference of limits $1\pi_1 - 1\pi_2$, the fact that the series constant for the ionised elements is four times that for neutral atoms suggested that the spark doublets of Group II , for example, would have approximately four times the separation of the doublets in the arc spectra of corresponding elements of Group I They gave the following figures in support —

Spark series, $\Delta\nu$		Arc series, $\Delta\nu'$		Ratio, $\Delta\nu/\Delta\nu'$	
Mg^+	91 5	Na	17 21	Mg^+ Na	=5 3
Ca^+	223	K	57 90	Ca^+ K	=3 9
Sr^+	800	Rb	237 71	Sr^+ Rb	=3 4
Ba^+	1691	Cs	554 10	Ba^+ Cs	=3 i
Zn^+	872	Cu	248 1	Zn^+ Cu	=3 5
Cd^+	2484	Ag	920 6	Cd^+ Ag	=2 7

The ratios show a systematic decrease with increase of atomic weight, but the question will doubtless be further investigated. Similar data were also given comparing the imperfectly known spark triplets of Group III with the arc triplets of Group II., showing ratios ranging from 2 2 to 5 0

An attempt to trace further numerical relations between the series of the ionised elements of Group II and the neutral elements of Group I has been made by Fues,† on the ground of Sommerfeld's theoretical deductions ("Atombau," pp 295, 511) In the extended Ritz formula, where the denominator is $[m+a+\alpha(m,a)+\alpha'(m,a)^2+\ ]^2$

* Verh. d D Phys Ges , 21, 240 (1919)
† Ann d Phys , 63, 1 (1920)

for arc spectra, and $[m+a^*+\alpha^*(m, a^*)+\ ]^2$ for enhanced series, it is considered that in a first approximation a^* for a singly-ionised atom of atomic number Z should have twice the value of a for the neutral atom of atomic number $Z-1$ In the sharp series $a=\sigma$, and in the principal series $a=\pi$, and with the Ritz numeration, having $m=1$ 5, in the sharp series, and $m=2$, 3, in the principal series, the constants for some of the spectra are as follows —

	σ, σ^*	π_1, $\pi_1{}^*$
Na	+0 15	+0 15
Mg^+	+0 43	+0 305
K	+0 325	+0 29
Ca^+	+0 70	+0 5±0 15
Rb	+0 31	+0 36
Sr^+	−0 815	+0 61±0 15
Cs	+0 45	+0 45
Ba^+	+0 93	+0 75

It will be seen that the relation is in some cases approximately fulfilled, but would not hold for the sharp series if integral values were assigned to m Investigations of this nature are evidently of importance in connection with theories of spectra, and may perhaps give indications as to the best type of series formula

The question of the relation of the spectral series to the grouping of the elements in the periodic table calls for much further investigation of the spectra which have not yet been resolved into series So far as the inquiry has gone, however, the results are very suggestive as to the kind of series to be expected in the spectrum of an element, and may be of considerable assistance in guiding further research.

APPENDIX I.

Calculation of Formula Constants

Probably the most generally useful formulæ are those of Ritz and Hicks, and it will suffice to indicate the methods of determining the constants in the case of the latter, namely

$$\nu = A - \frac{N}{\left(m+\mu+\frac{a}{m}\right)^2}$$

From the observational data it will be advisable, as a rule, to choose the wave-numbers of the two least refrangible lines, and one of the most refrangible, since the former have most effect on the second term and the latter have the greatest influence on the limit In all cases an approximate value of the limit should first be obtained by reference to Rydberg's interpolation table, as explained on p 28 When an approximate value of μ is also required, it may be obtained from the same source

Successive Approximation

Let ν_1, ν_2, ν_3 be the wave-numbers of three lines selected for the determination of constants, and let m, $m+p$, $m+q$ be the corresponding order-numbers Further, let

$$m\sqrt{\frac{N}{A-\nu_1}}=a\,,\quad (m+p)\sqrt{\frac{N}{A-\nu_2}}=b\,,\text{ and }(m+q)\sqrt{\frac{N}{A-\nu_3}}=c$$

Then a value of A has to be found which satisfies the relation

$$p(c-b)-(q-p)(b-a)=pq(q-p)$$

Beginning with the approximate value of A determined from Rydberg's table, a few trials will lead to the true value We then have

$$\mu=\frac{b-a}{p}-(2m+p)=\frac{c-b}{q-p}-(2m+p+q)$$

and

$$\alpha=a-m(m+\mu)=b-(m+p)(m+p+\mu)=c-(m+q)(m+q+\mu).$$

When three consecutive lines are selected, $p=1$ and $q=2$, and the relation to be satisfied by trials of A becomes

$$(c-b)-(b-a)=2$$

Hicks's Method

A more direct solution has been given by Hicks * An approximate value of A having been determined as before, the series is supposed given by

$$\nu = A+x-\frac{N}{\left(m+\mu+\frac{\alpha}{m}\right)^2}$$

* Phil. Mag., 30, 734 (1915).

where x is the correction to the limit, and x, μ, α are to be determined from three successive wave-numbers ν Binomial expansion gives

$$m+\mu+\frac{\alpha}{m}=\frac{\sqrt{N}}{(A-\nu+x)^{\frac{1}{2}}}=\frac{\sqrt{N}}{(A-\nu)^{\frac{1}{2}}}-\frac{\sqrt{N}}{2(A-\nu)^{\frac{3}{2}}}x=(m+d_m)-\gamma_m x \text{ (say)}$$

$$\therefore m\mu+\alpha=md_m-m\gamma_m x$$

Differencing,

$$\mu=\Delta(md_m)-x\Delta(m\gamma_m)$$
$$o=\Delta^2(md_m)-x\Delta^2(m\gamma_m),$$

whence

$$x=\frac{\Delta^2(md_m)}{\Delta^2(m\gamma_m)},$$

and μ and α are then easily calculated Hicks gives the following example from a series of oxygen lines in which the three consecutive wave-numbers are 10791 32, 16233 52, and 18753 65 The limit is $23{,}194+x$

(1)	10791 32		16233 52		18753 65	
(2)	12402 68		6960 48		4440 35	
(3)	4 0935156	$\bar{4}$ 37978	3 8426392	$\bar{4}$ 75610	3 6474172	$\bar{3}$ 04893
(4)	0 9465921	0 0002397	1 1974685	0 0005703	1 3926907	0 0011196
(5)	0 4732960	0 0001198	0 5987342	0 0002851	0 6963453	0 0005592
$\sqrt{\frac{N}{A-\nu}}$	2 973693		3 969484		4 969873	

1 947386			0 0002396			
	0 961066			0 0006157		
2 908452		0 009974	0 0008553		0 0007674	
	0 971040			0 0013831		
3 879492			0 0022384			

$$x=\frac{0\ 009974}{0\ 0007674}=13\ 00 \qquad A=23194\ 00+13\ 00=23207\ 00$$

$$\mu=0\ 961066-(13\times 0\ 0006157)$$
$$\underline{0\ 008004}$$
$$0\ 953062$$

$$\alpha=1\ 947386-13\times 0\ 0002396-2\mu \qquad 0\ 003114$$
$$1\ 909238 \qquad 1\ 906124$$
$$\underline{0\ 038148} \qquad \underline{1\ 909238}$$

$$\nu=23207\ 00-N/\left[m+0\ 953062+\frac{0\ 038148}{m}\right]^2$$

In each of the above main columns the first number is ν, the second $(A-\nu)$, the third log $(A-\nu)$, the fourth log $N/(A-\nu)$ obtained by subtracting the third from log. N (taken as 5 0401077 in the above example), the fifth is half the fourth, and the sixth is $\sqrt{N}/\sqrt{A-\nu}$, or $(m+d_m)$ The third is then subtracted from the

fifth and written down on the right, being the log. of $N^{\frac{1}{2}}/(A-\nu)^{\frac{1}{2}}$, below this is the antilog, which, divided by two, gives γ_m.

The decimal parts of $\sqrt{N}/\sqrt{(A-\nu)}$ at the bottom of the main columns are next multiplied by the respective integers m (in this case 2, 3, 4) and differenced twice. Similarly with the γ terms, the work being on the right. The constants are then readily determined.

A valuable feature of this method is that if the limits of error of the observations be known, their effects on the values of the constants can readily be found by calculating ∂x, $\partial\mu$, $\partial\alpha$.

When the term β/m^2 is introduced into the original formula, four lines are necessarily to be used, the d_m, γ_m are then to be multiplied by m^2, and differenced three times. Then

$$x=\frac{\Delta^3(m^2d_m)}{\Delta^3(m^2\gamma_m)}, \quad 2\mu=\Delta^2(m^2d_m)-x\Delta^2(m^2\gamma_m)$$

$$\alpha=\Delta(m^2d_m)-x\Delta(m^2\gamma_m)-(2m+1)\mu$$

$$\beta=m^2d_m-m^2\gamma_m x-m\alpha-m^2\mu$$

When wave-numbers are derived from data on the international scale the value of N should be taken as 109678·3, or log $N=5·0401208$.

The Differential Method

The differential method is generally applicable to series formulæ. In the case of the Hicks formula we have

$$\Delta\nu=\Delta A+\frac{2N}{\left(m+\mu+\frac{\alpha}{m}\right)^3}\left(\Delta\mu+\frac{\Delta\alpha}{m}\right)$$

Approximate values of A and μ being determined from Rydberg's table, and α being supposed zero, the values of $\Delta\nu$, being the differences between the observed and calculated wave-numbers, are obtained for the three lines selected for the determination of constants. The values of ΔA, $\Delta\mu$, and $\Delta\alpha$ ($=\alpha$ in this case) can then be determined from the three resulting linear equations. If α be large, it will be necessary to recalculate the constants, including an approximate value of α in the first equations when the $\Delta\nu$ are calculated.

When it is desired to investigate the value of N, four lines must be used, and a similar procedure adopted, with four equations of the form

$$\Delta\nu=\Delta A-\frac{\Delta N}{\left(m+\mu+\frac{\alpha}{m}\right)^2}+\frac{2N}{\left(m+\mu+\frac{\alpha}{m}\right)^3}\left(\Delta\mu+\frac{\Delta\alpha}{m}\right)$$

If a term β/m^2 be introduced into the original formula, the procedure is similar but rather more complex.

The differential method is obviously adapted for a least square solution, in which all the observed lines may be utilised in the calculation of constants. The numerical work involved, however, is rather laborious, and there is not much point in forcing a series of observations into an imperfect formula.

Determination of Limits in Special Cases

In the case of series which do not closely follow the formulae of Ritz or Hicks, other methods of determining the limits have to be adopted In a communication to the author, Prof Saunders has explained that his procedure is first to make some reasonable assumption as to the limit (say, from a graphical construction), and then to calculate the values of $[m+\mu+f(m)]$ from the corresponding terms $(A-\nu)$ for the later lines The values of $[\mu+f(m)]$ are then plotted against m, and if the curve shows an inflexion another limit is tried By successive trials the limit is thus obtained within a few units if several members of the series have been observed The result can often be checked by other series relationships, as, for instance, that the sharp and diffuse series must have the same limit, or that the first term of the principal series must correspond with the limit of the sharp series Combination of terms from different systems also gives an important check, as in the case of $1S-1p_2$ Saunders's plan is to adjust the limits so as to satisfy as many as possible of these conditions

The method adopted by Nicholson in the case of helium (*see* p 34) would probably also be useful in this connection, since it is possible to use all the lines of a series in calculating the limits

APPENDIX II.

TABLES FOR COMPUTATIONS

TABLE I —*Corrections to reduce Wave-lengths from Rowland's scale to the international scale*

Region	Subtract	Region	Subtract	Region	Subtract
λ 8800–8300	0 35	λ 6500–6050	0 21	λ 3450–3250	0 14
8300–8200	0 31	6050–5500	0 22	3250–3125	0 13
8200–8000	0 30	5500–5400	0 21	3125–2950	0 12
8000–7700	0 29	5400–5375	0 20	2950–2800	0 11
7700–7400	0 28	5375–5325	0 19	2800–2625	0 10
7400–7200	0 27	5325–5300	0 18	2625–2475	0 09
7200–7000	0 26	5300–5125	0 17	2475–2300	0 08
7000–6850	0 25	5125–4550	0 18	2300–2150	0 07
6850–6750	0 24	4550–4350	0 17	2150–1950	0 06
6750–6570	0 23	4350–4150	0 16		
6570–6500	0 22	4150–3450	0 15		

The corrections from 8800 to 7000 are as given by Meggers, the remainder are as given by Kayser At 10,000A the correction will be about 0 43A

TABLE IIA.—*Correction to Vacuum of Wave-lengths in Infra-Red*

The following corrections have been calculated from the Washington formula for 15° C and 760 mm It is not certain that the formula is accurately applicable to this region

λ in air	Add λ (μ—1)	Diff	λ in air.	Add λ (μ—1)	Diff
10,000	2 74		15,000	4 10	
		0 27			1 35
11,000	3 01		20,000	5 45	
		0 27			2 73
12,000	3 28		30,000	8 18	
		0 27			2 73
13,000	3 55		40,000	10 91	
		0 28			2 72
14,000	3 83		50,000	13 63	
		0 27			2 73
15,000	4 10		60,000	16 36	

TABLE II —*Correction to Vacuum of Wave-lengths in Air at 15° C and 760 mm*

λ in air	Add λ (μ—1)	Diff	λ in air	Add λ (μ—1)	Diff	λ in air.	Add λ (μ—1)	Diff
2000	0 6512		4500	1 2581		7400	2 0350	
		89			264			270
50	0 6601		4600	1 2845		7500	2 0620	
		94			265			271
2100	6695		4700	1 3110		7600	2 0891	
		96			265			270
50	0 6791		4800	1 3375		7700	2 1161	
		100			265			270
2200	0 6891		4900	1 3640		7800	2 1431	
		102			266			271
50	0 6993		5000	1 3906		7900	2 1702	
		104			267			270
2300	0 7097		5100	1 4173		8000	2 1972	
		107			266			271
50	0 7204		5200	1 4439		8100	2 2243	
		109			267			270
400	0 7313		5300	1 4706		8200	2 2513	
		222			267			271
2500	0 7535		5400	1 4973		8300	2 2784	
		229			267			270
2600	0 7764		5500	1 5240		8400	2 3054	
		233			268			271
2700	0 7997		5600	1 5508		8500	2 3325	
		238			267			271
2800	0 8235		5700	1 5775		8600	2 3596	
		241			268			271
2900	0 8476		5800	1 6043		8700	2 3867	
		245			268			270
3000	0 8721		5900	1 6311		8800	2 4137	
		247			269			271
3100	0 8968		6000	1 6580		8900	2 4408	
		249			268			271
3200	0 9217		6100	1 6848		9000	2 4679	
		252			269			271
3300	0 9469		6200	1 7117		9100	2 4950	
		253			269			271
3400	0 9722		6300	1 7386		9200	2 5221	
		255			269			271
3500	0 9977		6400	1 7655		9300	2 5492	
		256			269			271
3600	1 0233		6500	1 7924		9400	2 5763	
		257			269			272
3700	1 0490		6600	1 8193		9500	2 6035	
		259			269			271
3800	1 0749		6700	1 8462		9600	2 6306	
		259			270			271
3900	1 1008		6800	1 8732		9700	2 6577	
		260			269			271
4000	1 1268		6900	1 9001		9800	2 6848	
		262			270			271
4100	1 1530		7000	1 9271		9900	2 7119	
		262			270			272
4200	1·1792		7100	1 9541		10000	2 7391	
		262			270			
4300	1 2054		7200	1 9811				
		263			269			
4400	1 2317		7300	2 0080				
		264						

$\lambda_{vac.} = \mu\lambda_{air}$ $\Delta\lambda = \lambda_{vac} - \lambda_{air} = \lambda_{air}(\mu - 1)$.

TABLE III.—*Rydberg's Interpolation Table (revised).*

Values of the Function $109678\ 3/(m+\mu)^2$.

μ	1	Δ_1	2	Δ_2	3	Δ_3	4	Δ_4	5	Δ_5	6	Δ_6	7	Δ_7	8	Δ_8	9	μ
0·00	109678	*82258*	27420	*15233*	12187	*5332*	6855	*2468*	4387	*1340*	3047	*809*	2238	*524*	1714	*360*	1354	0·00
0 01	107517	*80370*	27147	*15041*	12106	*5285*	6821	*2461*	4370	*1333*	3037	*805*	2232	*523*	1709	*358*	1351	0 01
0 02	105419	*78540*	26879	*14853*	12026	*5239*	6787	*2435*	4352	*1326*	3026	*801*	2225	*520*	1705	*357*	1348	0 02
0·03	103382	*76767*	26615	*14669*	11946	*5193*	6753	*2418*	4335	*1319*	3016	*797*	2219	*518*	1701	*356*	1345	0 03
0·04	101404	*75049*	26355	*14487*	11868	*5148*	6720	*2402*	4318	*1312*	3006	*793*	2213	*516*	1697	*355*	1342	0·04
0 05	99481	*73383*	26098	*14308*	11790	*5103*	6687	*2386*	4301	*1304*	2997	*790*	2207	*514*	1693	*354*	1339	0 05
0·06	97613	*71767*	25846	*14133*	11713	*5059*	6654	*2370*	4284	*1297*	2987	*787*	2200	*512*	1688	*352*	1336	0 06
0·07	95797	*70200*	25597	*13960*	11637	*5016*	6621	*2354*	4267	*1290*	2977	*783*	2194	*510*	1684	*351*	1333	0·07
0·08	94031	*68680*	25351	*13789*	11562	*4973*	6589	*2339*	4250	*1283*	2967	*779*	2188	*508*	1680	*350*	1330	0·08
0 09	92314	*67205*	25109	*13622*	11487	*4930*	6557	*2324*	4233	*1276*	2957	*775*	2182	*506*	1676	*349*	1327	0 09
0 10	90643	*65773*	24870	*13457*	11413	*4888*	6525	*2308*	4217	*1269*	2948	*772*	2176	*504*	1672	*347*	1325	0 10
0 11	89017	*64382*	24635	*13296*	11339	*4847*	6492	*2292*	4200	*1262*	2938	*768*	2170	*502*	1668	*346*	1322	0 11
0 12	87435	*63032*	24403	*13136*	11267	*4806*	6461	*2277*	4184	*1256*	2928	*765*	2163	*500*	1663	*344*	1319	0 12
0 13	85894	*61719*	24175	*12980*	11195	*4765*	6430	*2262*	4168	*1249*	2919	*762*	2157	*498*	1659	*343*	1316	0 13
0 14	84394	*60445*	23949	*12825*	11124	*4725*	6399	*2248*	4151	*1242*	2909	*758*	2151	*496*	1655	*342*	1313	0 14
0 15	82933	*59206*	23727	*12674*	11053	*4685*	6368	*2233*	4135	*1235*	2900	*755*	2145	*494*	1651	*341*	1310	0 15
0 16	81509	*58001*	23508	*12524*	10984	*4646*	6338	*2219*	4119	*1228*	2891	*752*	2139	*492*	1647	*340*	1307	0 16
0 17	80122	*56830*	23292	*12377*	10915	*4608*	6307	*2204*	4103	*1222*	2881	*748*	2133	*490*	1643	*339*	1304	0 17
0 18	78769	*55691*	23078	*12232*	10846	*4569*	6277	*2189*	4088	*1216*	2872	*744*	2128	*489*	1639	*337*	1302	0 18
0 19	77451	*54583*	22868	*12090*	10778	*4531*	6247	*2175*	4072	*1209*	2863	*741*	2122	*487*	1635	*336*	1299	0 19
0 20	76166	*53505*	22661	*11950*	10711	*4494*	6217	*2161*	4056	*1203*	2853	*737*	2116	*485*	1631	*335*	1296	0 20
0 21	74912	*52456*	22456	*11812*	10644	*4456*	6188	*2147*	4041	*1197*	2844	*734*	2110	*483*	1627	*334*	1293	0 21
0 22	73689	*51435*	22254	*11676*	10578	*4419*	6159	*2134*	4025	*1190*	2835	*731*	2104	*481*	1623	*333*	1290	0 22
0 23	72495	*50440*	22055	*11542*	10513	*4383*	6130	*2120*	4010	*1184*	2826	*728*	2098	*479*	1619	*332*	1287	0 23
0 24	71331	*49472*	21859	*11411*	10448	*4347*	6101	*2107*	3994	*1177*	2817	*725*	2092	*477*	1615	*331*	1284	0 24
0 25	70194	*48529*	21665	*11281*	10384	*4312*	6072	*2093*	3979	*1171*	2808	*721*	2087	*475*	1612	*330*	1282	0 25
0 26	69084	*47611*	21473	*11153*	10320	*4276*	6044	*2080*	3964	*1165*	2799	*718*	2081	*473*	1608	*329*	1279	0 26
0 27	68001	*46716*	21285	*11028*	10257	*4242*	6015	*2066*	3949	*1159*	2790	*715*	2075	*471*	1604	*328*	1276	0 27
0 28	66942	*45844*	21098	*10903*	10195	*4208*	5987	*2053*	3934	*1153*	2781	*712*	2069	*469*	1600	*326*	1274	0 28
0 29	65909	*44994*	20915	*10782*	10133	*4174*	5959	*2040*	3919	*1147*	2772	*708*	2064	*468*	1596	*325*	1271	0 29
0 30	64898	*44165*	20733	*10662*	10071	*4139*	5932	*2028*	3904	*1141*	2763	*705*	2058	*466*	1592	*324*	1268	0 30
0 31	63911	*43357*	20554	*10543*	10011	*4106*	5905	*2015*	3890	*1135*	2755	*702*	2053	*465*	1588	*323*	1265	0 31
0 32	62947	*42570*	20377	*10427*	9950	*4073*	5877	*2002*	3875	*1129*	2746	*699*	2047	*463*	1584	*321*	1263	0 32
0 33	62004	*41801*	20203	*10312*	9891	*4041*	5850	*1989*	3861	*1124*	2737	*696*	2041	*461*	1580	*320*	1260	0 33
0 34	61086	*41055*	20031	*10199*	9832	*4009*	5823	*1977*	3846	*1117*	2729	*693*	2036	*459*	1577	*320*	1257	0 34

μ	1	$\Delta\nu$	2	$\Delta\nu$	3	$\Delta\nu$	4	$\Delta\nu$	5	$\Delta\nu$	6	$\Delta\nu$	7	$\Delta\nu$	8	$\Delta\nu$	9	μ
0 35	60180	*40320*	19860	*10087*	9773	*3977*	5796	*1964*	3832	*1112*	2720	*690*	2030	*457*	1573	*319*	1254	0 35
0 36	59298	*39606*	19692	*9977*	9715	*3945*	5770	*1952*	3818	*1106*	2712	*687*	2025	*455*	1570	*318*	1252	0 36
0 37	58436	*38910*	19526	*9869*	9657	*3914*	5743	*1940*	3803	*1100*	2703	*684*	2019	*453*	1566	*317*	1249	0 37
0 38	57592	*38229*	19363	*9763*	9600	*3883*	5717	*1928*	3789	*1094*	2695	*681*	2014	*452*	1562	*315*	1247	0 38
0 39	56766	*37564*	19202	*9658*	9544	*3853*	5691	*1916*	3775	*1089*	2686	*678*	2008	*450*	1558	*314*	1244	0 39
0 40	55958	*36916*	19042	*9554*	9488	*3823*	5665	*1904*	3761	*1083*	2678	*675*	2003	*449*	1554	*313*	1241	0 40
0 41	55167	*36283*	18884	*9452*	9432	*3793*	5639	*1892*	3747	*1078*	2669	*672*	1997	*447*	1550	*312*	1238	0 41
0 42	54393	*35665*	18728	*9351*	9377	*3763*	5614	*1880*	3734	*1073*	2661	*669*	1992	*445*	1547	*311*	1236	0 42
0 43	53635	*35061*	18574	*9252*	9322	*3733*	5589	*1869*	3720	*1067*	2653	*666*	1987	*444*	1543	*310*	1233	0 43
0 44	52893	*34471*	18422	*9154*	9268	*3704*	5564	*1857*	3707	*1062*	2645	*663*	1982	*442*	1540	*309*	1231	0 44
0 45	52166	*33894*	18272	*9057*	9215	*3676*	5539	*1846*	3693	*1057*	2636	*660*	1976	*440*	1536	*308*	1228	0 45
0 46	51454	*33330*	18124	*8962*	9162	*3648*	5514	*1835*	3679	*1051*	2628	*658*	1970	*438*	1532	*307*	1225	0 46
0 47	50756	*32778*	17978	*8869*	9109	*3620*	5489	*1823*	3666	*1046*	2620	*655*	1965	*436*	1529	*306*	1223	0 47
0 48	50072	*32239*	17833	*8776*	9057	*3592*	5465	*1812*	3653	*1041*	2612	*652*	1960	*435*	1525	*305*	1220	0 48
0 49	49402	*31712*	17690	*8685*	9005	*3565*	5440	*1801*	3639	*1035*	2604	*649*	1955	*433*	1522	*304*	1218	0 49
0 50	48746	*31197*	17549	*8596*	8953	*3537*	5416	*1790*	3626	*1030*	2596	*646*	1950	*432*	1518	*303*	1215	0 50
0 51	48102	*30693*	17409	*8507*	8902	*3510*	5392	*1779*	3613	*1025*	2588	*643*	1945	*430*	1515	*302*	1213	0 51
0 52	47472	*30201*	17271	*8419*	8852	*3484*	5368	*1769*	3599	*1019*	2580	*641*	1939	*428*	1511	*301*	1210	0 52
0 53	46854	*29719*	17135	*8333*	8803	*3457*	5345	*1759*	3586	*1014*	2572	*638*	1934	*427*	1507	*300*	1207	0 53
0 54	46247	*29247*	17000	*8248*	8752	*3431*	5321	*1748*	3573	*1009*	2564	*635*	1929	*425*	1504	*299*	1205	0 54
0 55	45652	*28785*	16867	*8164*	8703	*3405*	5298	*1737*	3561	*1004*	2557	*633*	1924	*424*	1500	*298*	1202	0 55
0 56	45068	*28332*	16736	*8082*	8654	*3379*	5275	*1727*	3548	*999*	2549	*630*	1919	*422*	1497	*297*	1200	0 56
0 57	44496	*27890*	16606	*8000*	8606	*3354*	5252	*1717*	3535	*994*	2541	*627*	1914	*421*	1493	*296*	1197	0 57
0 58	43935	*27458*	16477	*7919*	8558	*3329*	5229	*1707*	3522	*989*	2533	*624*	1909	*419*	1490	*295*	1195	0 58
0 59	43384	*27034*	16350	*7840*	8510	*3304*	5206	*1696*	3510	*984*	2526	*622*	1904	*418*	1486	*294*	1192	0 59
0 60	42843	*26618*	16225	*7762*	8463	*3280*	5183	*1686*	3497	*979*	2518	*619*	1899	*416*	1483	*293*	1190	0 60
0 61	42313	*26212*	16101	*7685*	8416	*3255*	5161	*1676*	3485	*975*	2510	*616*	1894	*414*	1480	*292*	1188	0 61
0 62	41792	*25814*	15978	*7608*	8370	*3231*	5139	*1666*	3473	*970*	2503	*614*	1889	*413*	1476	*291*	1185	0 62
0 63	41281	*25424*	15857	*7533*	8324	*3208*	5116	*1656*	3460	*965*	2495	*611*	1884	*411*	1473	*290*	1183	0 63
0 64	40779	*25042*	15737	*7459*	8278	*3184*	5094	*1646*	3448	*961*	2487	*608*	1879	*410*	1469	*289*	1180	0 64
0 65	40286	*24668*	15618	*7385*	8233	*3161*	5072	*1636*	3436	*956*	2480	*606*	1874	*408*	1466	*288*	1178	0 65
0 66	39802	*24301*	15501	*7313*	8188	*3137*	5051	*1627*	3424	*951*	2473	*604*	1869	*407*	1462	*287*	1175	0 66
0 67	39327	*23942*	15385	*7242*	8143	*3114*	5029	*1617*	3412	*947*	2465	*601*	1864	*405*	1459	*286*	1173	0 67
0 68	38860	*23589*	15271	*7172*	8099	*3091*	5008	*1608*	3400	*942*	2458	*598*	1860	*404*	1456	*285*	1171	0 68
0 69	38401	*23244*	15157	*7102*	8055	*3069*	4986	*1598*	3388	*937*	2451	*596*	1855	*403*	1452	*284*	1168	0 69

TABLE III (*continued*)—*Rydberg's Interpolation Table* (*revised*)

Values of the Function $109678\ 3/(m+\mu)^2$

μ	1	$\Delta\nu$	2	$\Delta\nu$	3	$\Delta\nu$	4	$\Delta\nu$	5	$\Delta\nu$	6	$\Delta\nu$	7	$\Delta\nu$	8	$\Delta\nu$	9	μ
0·70	37951	*22906*	15045	*7034*	8011	*3046*	4965	*1589*	3376	*933*	2443	*593*	1850	*401*	1449	*283*	1166	0·70
0·71	37508	*22574*	14934	*6966*	7968	*3024*	4944	*1580*	3364	*928*	2436	*591*	1845	*400*	1445	*282*	1163	0·71
0·72	37074	*22249*	14825	*6899*	7926	*3003*	4923	*1571*	3352	*923*	2429	*589*	1840	*398*	1442	*281*	1161	0·72
0·73	36646	*21930*	14716	*6833*	7883	*2981*	4902	*1562*	3340	*918*	2422	*586*	1836	*397*	1439	*280*	1159	0·73
0·74	36226	*21617*	14609	*6768*	7841	*2959*	4882	*1553*	3329	*915*	2414	*583*	1831	*395*	1436	*280*	1156	0·74
0·75	35813	*21310*	14503	*6704*	7799	*2938*	4861	*1544*	3317	*910*	2407	*581*	1826	*393*	1433	*279*	1154	0·75
0·76	35408	*21010*	14398	*6640*	7758	*2917*	4841	*1535*	3306	*906*	2400	*579*	1821	*392*	1429	*278*	1151	0·76
0·77	35009	*20815*	14294	*6577*	7717	*2897*	4820	*1526*	3294	*901*	2393	*576*	1817	*391*	1426	*277*	1149	0·77
0·78	34616	*20424*	14192	*6516*	7676	*2876*	4800	*1517*	3283	*897*	2386	*574*	1812	*389*	1423	*276*	1147	0·78
0·79	34231	*20141*	14090	*6454*	7636	*2856*	4780	*1508*	3272	*893*	2379	*572*	1807	*388*	1419	*275*	1144	0·79
0·80	33851	*19861*	13990	*6394*	7596	*2836*	4760	*1500*	3260	*888*	2372	*569*	1803	*387*	1416	*274*	1142	0·80
0·81	33478	*19588*	13890	*6334*	7556	*2815*	4741	*1492*	3249	*884*	2365	*567*	1798	*385*	1413	*273*	1140	0·81
0·82	33111	*19319*	13792	*6276*	7516	*2795*	4721	*1483*	3238	*880*	2358	*564*	1794	*384*	1410	*273*	1137	0·82
0·83	32751	*19056*	13695	*6218*	7477	*2776*	4701	*1474*	3227	*876*	2351	*562*	1789	*382*	1407	*272*	1135	0·83
0·84	32396	*18798*	13598	*6160*	7438	*2756*	4682	*1466*	3216	*872*	2344	*560*	1784	*380*	1404	*271*	1133	0·84
0·85	32046	*18543*	13503	*6104*	7399	*2736*	4663	*1458*	3205	*868*	2337	*557*	1780	*379*	1401	*270*	1131	0·85
0·86	31703	*18294*	13409	*6048*	7361	*2717*	4644	*1450*	3194	*864*	2330	*555*	1775	*378*	1397	*269*	1128	0·86
0·87	31364	*18048*	13316	*5993*	7323	*2698*	4625	*1442*	3183	*859*	2324	*553*	1771	*377*	1394	*268*	1126	0·87
0·88	31032	*17809*	13223	*5938*	7285	*2679*	4606	*1434*	3172	*855*	2317	*551*	1766	*375*	1391	*267*	1124	0·88
0·89	30704	*17572*	13132	*5884*	7248	*2661*	4587	*1425*	3162	*851*	2311	*549*	1762	*374*	1388	*267*	1121	0·89
0·90	30382	*17340*	13042	*5831*	7211	*2643*	4568	*1417*	3151	*847*	2304	*547*	1757	*372*	1385	*266*	1119	0·90
0·91	30065	*17113*	12952	*5778*	7174	*2625*	4549	*1409*	3140	*843*	2297	*544*	1753	*371*	1382	*265*	1117	0·91
0·92	29752	*16889*	12863	*5725*	7138	*2607*	4531	*1402*	3129	*839*	2290	*541*	1749	*370*	1379	*264*	1115	0·92
0·93	29445	*16669*	12776	*5674*	7102	*2589*	4513	*1394*	3119	*835*	2284	*540*	1744	*369*	1375	*263*	1112	0·93
0·94	29142	*16453*	12689	*5624*	7065	*2571*	4494	*1386*	3108	*831*	2277	*537*	1740	*368*	1372	*262*	1110	0·94
0·95	28844	*16241*	12603	*5573*	7030	*2554*	4476	*1378*	3098	*827*	2271	*535*	1736	*367*	1369	*261*	1108	0·95
0·96	28550	*16032*	12518	*5524*	6994	*2536*	4458	*1370*	3088	*824*	2264	*533*	1731	*365*	1366	*260*	1106	0·96
0·97	28261	*15827*	12434	*5475*	6959	*2519*	4440	*1363*	3077	*819*	2258	*531*	1727	*364*	1363	*260*	1103	0·97
0·98	27976	*15625*	12351	*5437*	6924	*2501*	4423	*1356*	3067	*816*	2251	*529*	1722	*362*	1360	*259*	1101	0·98
0·99	27696	*15428*	12268	*5379*	6889	*2484*	4405	*1348*	3057	*812*	2245	*527*	1718	*361*	1357	*258*	1099	0·99
1·00	27420	*15233*	12187	*5332*	6855	*2468*	4387	*1340*	3047	*809*	2238	*524*	1714	*360*	1354	*257*	1097	1·00

PART II.

TABLES OF SERIES LINES.

CHAPTER X.

EXPLANATION OF TABLES.

The construction of the tables of spectra which follow may be gathered from the descriptions of series which have already been given, but a brief summary of the main points may not be superfluous

The wave-number of a series line usually appears as the difference of two wave-numbers, one of which is the limit of the series to which it belongs The lines of any one series are represented by the differences between the limit and a number of *terms* forming a *sequence*, the sequence being of the form $N/[f(m)]^2$, where N is the Rydberg constant as determined from hydrogen, and $f(m)$ is of the form *m plus* a fraction The fractional part for successive lines is not constant, but varies with m, and the fraction may be represented approximately by the terms $(\mu+\alpha/m)$ of the Hicks formula, or by the corresponding terms of other formulæ

When the limit of a series has been ascertained, the actual values of the terms of the sequence can be determined, independently of formulæ, by subtracting the wave-numbers of the observed lines from the wave-number representing the limit Other terms of the sequence may be approximately calculated by the use of a formula when required

The limit of a series appears as one of the terms of the sequence of another series Thus the four chief series are represented by

		Limits		Terms
$p(m)$	=	$1s$	—	mp
$s(m)$	=	$1p$	—	ms
$d(m)$	=	$1p$	—	md
$f(m)$	=	$2d$	—	mf

As expressed in the combination principle, other series, or other lines, may appear corresponding to other combinations of terms from the various sequences, as $2s-mp$, $2p-md$, and so on For the analysis of a spectrum, whereby it is sought to associate as many lines as possible in a connected system, the terms of the four chief series are first determined, and afterwards utilised in a search for combinations The procedure which has been adopted in recent years has accordingly been to rely upon formulæ mainly for the determination of the limit, or limits, of one of the chief series The limits of the other chief series are then obtained by the aid of the Rydberg-Schuster and Runge laws, as illustrated on p 24, and when these have been determined, the terms are derived by subtracting the wave-numbers of the observed lines from the respective limits

In the tables, the wave-lengths, intensities, and wave-numbers of the observed lines of the four chief series are first given, followed by the separations in the case of doublets and triplets, and finally by the terms Singlet, doublet and triplet series are distinguished respectively by capital, Greek and small letter abbreviations. Single lines which are derived by combination from doublet or triplet terms, however, are necessarily indicated by the symbols of the series from which they originate. Combinations cannot conveniently be represented by single letters, but their relations to the main series are readily shown by differences such as $2\delta-m\pi$, $1S-mp$, and so on

The components of pairs and triplets, and the structure of members of the diffuse

series, are indicated by appropriate groupings of the lines Unrecorded components or satellites are indicated, where necessary, by a dash (—) When two or more lines are available for the determination of a term the mean has been taken When no intensity is stated it may usually be assumed, except for infra-red lines, that the intensity is low.

The wave-lengths from $\lambda 10000A$ to the ultra-violet are on the international scale unless otherwise stated. When the original determinations were on the Rowland scale they have been corrected by Table I In the calculation of wave-numbers, the wave-lengths were corrected to vacuum by the Washington tables (Table II) and the reciprocals taken

Wave-lengths in the infra-red greater than $10000A$ are on Rowland's scale, unless otherwise stated, as the correction to the international system has only a slight effect on the wave-numbers In view of the uncertainty as to the corrections to vacuum, the published wave-numbers have been adopted

In the examples of formulæ which have been introduced, the series constant has been taken throughout as 109678 3, except for helium Bohr's theory suggests a special value for each element, depending on the atomic weight (see p 64), but the range is small, and the accuracy with which the lines are represented would scarcely be affected, if at all

In the compilation of many of the tables, much assistance has been derived from reports on the admirable work carried on under the direction of Prof Paschen which have been given by Dunz* and Lorenser.†

* B Dunz "Bearbeitung unserer Kenntnisse von den Serien" Dissertation, Tubingen, (1911)

† E Lorenser, "Beiträge zur Kenntnis der Bogenspektren der Erdalkalien." Dissertation Tubingen (1913)

CHAPTER XI

HYDROGEN AND HELIUM

The spectra of hydrogen and helium have unusual features, and it will be convenient to refer to them apart from the general groups of elements

HYDROGEN

H. At wt =1, At No =1

In the vacuum tube spectrum of hydrogen there are usually two spectra superposed, one called the *primary* spectrum, which includes the Balmer series, and the other called the *secondary* spectrum, consisting of a great number of comparatively faint lines The latter appears to consist, in part at least, of the components of a band spectrum, but it has not yet been completely analysed, and is not considered in the appended table

The primary spectrum, as already explained (p 14) does not form an ordinary system of series, but is represented closely by the formula

$$\nu = 109678\ 3\left(\frac{1}{m_1^2} - \frac{1}{m^2}\right)$$

When $m_1=1$, the formula gives lines in the Schumann region observed by Lyman, $m_1=2$ gives the Balmer series, and $m_1=3$ gives a series in the infra-red which was predicted by Ritz and partially observed by Paschen

The lines of the Balmer series designated H_α, H_β, are very close doublets, the separations in wave-length being respectively 0 14A and 0 08 4, according to Michelson, the less refrangible components being the stronger In a recent Paper, Merton* has described experiments on mixtures of hydrogen and helium, which show that each of these lines probably consists of three components, which exhibit great variations in their relative intensities under different conditions The exact nature of these changes has not been completely determined, but the results are probably not inconsistent with Sommerfeld's theory of the fine structure of the lines

Careful measurements of the first six lines of the Balmer series in an unresolved condition have been made by W E Curtis (p 27), who found that the " centres of gravity " of the lines could not be represented within the limits of error by the simple formula given above

The formula,

$$\nu = 109678\ 28\left[\frac{1}{(2-0\ 00000383)^2} - \frac{1}{(m+0\ 00000210)^2}\right]$$

was found by Curtis to represent the six observed lines with no error exceeding 0 001A, and the remaining lines with errors which probably do not exceed those of observation The wave-lengths tabulated below have been calculated from this formula, and are the values in I A units (*i e*, in air at 15°C and 760 mm) In calculating the infra-red and ultra-violet series, it has been assumed that they may be regarded as combinations derived from terms of the Balmer series

Paschen's wave-lengths† for the first four lines of the Balmer series are 6562·797,

* Proc Roy Soc, A **97**, 307 (1920).
† Ann d Phys, **51**, No 7 (1916)

4861 326, 4340 465, 4101 735 A discussion of these, in conjunction with Curtis's measures, has led H Bell* to suggest 109677 9 as the value of the Rydberg constant N.

In an extension of Bohr's theory, J Ishiwara† has given a formula for the hydrogen series which is written

$$\nu = N\left(\frac{1}{n_1^2-\sigma} - \frac{1}{n_2^2-\sigma}\right)$$

where the theoretical value of $\sigma = 3\,942 \times 10^{-5}$ From Curtis's wave-lengths for the first six lines of the Balmer series, Ishiwara found the mean value of N to be 109678 05 The individual values (decimal parts) were 0 06, 0 01, 0 00, 0 04, 0 07, 0 10, showing an appreciably smaller range than those deduced from the simple Balmer formula

H Balmer Series
Limit = A = 27419 674

m	λ, $I\,A$	ν	$A-\nu$
1	—	—	109677 82
2	—	—	27419 512
3	6562 793	15233 216	12186 458
4	4861 327	20564 793	6854 881
5	4340 466	23032 543	4387 131
6	4101 738	24373 055	3046 619
7	3970·075	25181 343	2238 331
8	3889 052	25705 957	1713 717
9	3835 387	26065 61	1354 06
10	3797 900	322 90	1096 77
11	70 633	513 24	906 43
12	50 154	658·03	761 64
13	34 371	770 68	648 99
14	21 941	860·09	559 58
15	11 973	932 21	487 46
16	03 855	991 24	428 43
17	3697 154	27040 16	379 51
18	91 557	81 16	338 51
19	86 834	27115 85	303 82
20	82 810	45 47	274 20
21	79 355	70 96	248 71
22	76 365	93·07	226 60
23	73 761	27212 35	207 32
24	71 478	29 26	190 41
25	69 466	44 19	175 48
26	67 684	57 42	162 25
27	66 097	69 23	150 44
28	64 679	79 78	139 89
29	63 405	89 26	130 41
30	62 258	97 81	121 86
31	61 221	27305 54	114 13
32	60 280	12 55	107 12
33	59 423	18 94	100 73
34	58 641	24 79	94 88
35	57 926	30 14	89 53
36	57 269	35 05	84 62
37	56 666	39 55	80·12
∞	45 981	27419 674	0

H Infra-Red Series
Limit = A = 12186 46

m	λ air	λ vac	ν	$A-\nu$
4	18751 05	18756 17	5331 58	6854 88
5	12818 11	12821 61	7799 33	4387 13

Paschen's observed values, on Rowland's scale, are 18751 3, 12817 6, these give ν_4 = 5331 53 and ν_5 = 7799 67

H Ultra-Violet Series
Limit = A = 109677 82

m	λ vac	ν	$A-\nu$
2	1215 68	82258 31	27419 51
3	1025 83	97481 36	12186 46
4	972 54	102822 94	6854 88

The wave-lengths, in vacuo, as observed by Lyman, are 1216 0, 1026 0, 972 7
Millikan finds 1215 7 for the first line

Note.—The provisional wave-lengths given by Wood for the nine lines of the Balmer series first observed by him in the laboratory spectrum are as follows —

λ R		λ $I\,A$
3722 12		3721 97
12 22		12 07
03 92		03 77
3697 35		3697 20
91 72		91 57
86 99	.	86 84
82 96	...	82 81
79 46	..	79 31
3676 44	. .	76 29

* Phil Mag, **40**, 489 (1920).
† Math & Phys Soc, Tokyo, Series 2, **8**, 179 (1915)

Helium.

He At wt =4, At No =2

The line spectrum of helium, as observed ordinarily in vacuum tubes, consists of a system of singlet series and a system of doublets The doublets are very close, the wave-number separation being about 1 02, so that in the principal series only the first member has been resolved, and only the earlier members of the sharp and diffuse series. The doublets are somewhat unusual, inasmuch as in the sharp and diffuse series the stronger component is on the more refrangible side, while the first principal line has its stronger component on the side of greater wave-length The weaker components are also unusually faint in comparison with the chief lines

The majority of the measurements are by Runge and Paschen,* but the more recent interferometer values determined by Merrill at the Bureau of Standards, Washington,† have been substituted for 21 lines, the greatest error in these values is believed not to exceed 0 003 *A* In the case of doublets, the Washington values refer to the stronger components, and the wave-lengths of the companion lines have been adjusted to show the same separations as those indicated by Runge and Paschen's values The infra-red wave-lengths are by Paschen ‡ The last two lines in the principal series of doublets are due to Schniederjost §

It should be noted that the resolution of the spectrum into two systems of series was regarded by some as indicating the presence of two gases, which were distinguished as helium and parhelium, giving the doublet and singlet systems respectively There is now no reason to believe that helium is other than a single element, but the name " parhelium " has to some extent survived In connection with his work on stellar spectra, Lockyer re-named this pseudo-element " asterium " The doublet and singlet systems are also sometimes distinguished as He I and He II respectively.

The following Hicks formula has been calculated from the three lines of the sharp series of singlets measured at Washington —

$$S(m)=27175\ 17-\frac{109723\ 2}{\left(m+0\ 862157-\frac{0\ 010908}{m}\right)^2}$$

As will be seen from the following list of the differences " observed *minus* calculated " wave-numbers, the formula represents all but the first line with considerable accuracy Lines marked with an asterisk were used in the calculation of constants

m	$O-C$ ($\Delta\nu$)	m	$O-C$ ($\Delta\nu$)	m	$O-C$ ($\Delta\nu$)
1	−16 4	5	+0 10	9	+0 49
2	0 00*	6	+0 14	10	not observed
3	0 00*	7	+0 52	11	−0 02
4	0 00*	8	+0 35	12	+1 85

The later lines were probably less accurately measured than the earlier ones in consequence of their low intensities.

For the doublet system, the following formula for the stronger components of

* Astrophys Jour, **3**, 4 (1896)
† Astrophys Jour, **46**, 357 (1917)
‡ Ann d Phys, **27**, 537 (1908), **29**, 628 (1909)
§ Zeit f Wiss Phot, **2**, 265 (1904)

the diffuse series has been calculated from the first, third and fifth lines as measured at Washington —

$$\delta_1(m) = 29223\ 88 - \frac{109723\ 2}{\left(m + 0\ 996982 + \frac{0\ 001695}{m}\right)^2}$$

giving the following residuals —

m	$O-C(\Delta\nu)$	m	$O-C(\Delta\nu)$	m	$O-C(\Delta\nu)$
2	+0 02*	8	−0 08	14	+0 08
3	−0 06	9	−0 22	15	+0 33
4	0 00*	10	−0 08	16	+0 30
5	+0 02	11	+0 09	17	−1 7 ?
6	0 00*	12	+0 13	18	+1 2
7	0 00	13	+0 01		

The limits of other main series were deduced by the application of the Rydberg-Schuster and Runge laws All the observed lines are either included in the main series of singlets or doublets or are accounted for as combinations

Several combination series are observed in the helium spectrum when the gas is subjected to strong electric fields The first of these was recorded by Koch,* and others have been observed by Merton,† Stark‡ and Liebert § The wave-lengths of most of these lines have only been roughly measured, and the wave-lengths calculated from the combinations have therefore been inserted in the tables for comparison with the observations

Besides the line spectrum, there is an interesting band spectrum of helium, which is well developed under appropriate experimental conditions || It was found by Fowler¶ that the heads of some of the stronger bands, in contrast with all other known band spectra, are arranged in accordance with the laws of line-series There is, however, no apparent relation between the band- and line-series, except that the main series of bands runs nearly parallel to the principal series of helium doublets Thus, a displacement of the latter towards the red by a wave-number interval of 4159 would nearly superpose it on the stronger heads of the main set of bands

Ionised Helium (He^+)

Under the action of strong discharges, as already mentioned ,helium yields another system of lines for which the series constant has rather more than four times the value deduced from hydrogen Otherwise the series resemble those of hydrogen, and can be represented closely by an equally simple formula, namely,

$$\nu = 4N'\left(\frac{1}{m_1^2} - \frac{1}{m^2}\right)$$

where N' has the value 109723 22 as compared with 109678 3 for hydrogen

* Ann d Phys , **48**, 98 (1915).
† Proc Roy Soc , A **95**, 30 (1918)
‡ Ann d Phys , **56**, 577 (1918)
§ Ann d Phys , **56**, 600-617 (1918)
|| W E Curtis, Proc Roy Soc , A **89**, 146 (1913) E Goldstein, Verh d Deutsch Phys-Gesell , **15**, 402 (1913)
¶ Proc Roy Soc , A **91**, 208 (1915)

Helium, Doublet System

Principal $1\sigma - m\pi$
$1\sigma = 38454\ 71$

λ, Int	ν	Δν	m	$m\pi_{2,1}$
*10829 09 } (200)	9231 86	1 03	(1)	29222 85
*10830 30 }	9230 83			29223 88
†3888 646 (10)	25708 63		(2)	12746 08
†3187 743 (8)	31361 12		(3)	7093 59
†2945 104 (6)	33944 75		(4)	4509 96
2829 06 (4)	35337 05		(5)	3117 66
2763 80 (2)	36171 40		(6)	2283 31
2723 18 (1)	36710 92		(7)	1743 79
2696 13 (1)	37079 21		(8)	1375 50
2677 1 (1)	37342 7		(9)	1112 0
2663 2 (1)	37537 5		(10)	917 2
2652 95	37682 67		(11)	772 04
2644 84	37798 22		(12)	656 49

Sharp $1\pi - m\sigma$
$1\pi_2 = 29222\ 85$, $1\pi_1 = 29223\ 88$

λ, Int	ν	Δν	m	mσ
—10829 09 } (200)	— 9231 86	1 03	(1)	38454 71
—10830 10 }	— 9230 83			
7065 677 (1)	14149 03	0 98	(2)	15073 87
†7065 185 (5)	14150 01			
4713 366 (1)	21210 34	1 01	(3)	8012 53
†4713 143 (3)	21211 35			
4120 981 (1)	24259 24	1 01	(4)	4963 63
†4120 812 (3)	24260 25			
3867 62 (1)	25848 40	1 06	(5)	3374 42
3867 46 (2)	25849 46			
3732 99 (1)	26780 58	1 01	(6)	2442 29
3732 85 (1)	26781 59			
3652 12 (1)	27373 58	0 90	(7)	1849 40
3652 00 (1)	27374 48			
3599 46 (1)	27774 05	1 06	(8)	1448 77
3599 32 (1)	27775 11			
3562 98 (1)	28058 41		(9)	1165 47
3536 81 (1)	28265 96		(10)	957 92
3517 33 (1)	28422 56		(11)	801 32
3502 32 (1)	28544 37		(12)	679 51
3490 62 (1)	28640 04		(13)	583 84
3481 4	28715 8		(14)	508 1

Diffuse $1\pi - m\delta$
$1\pi_2 = 29222\ 85$, $1\pi_1 = 29223\ 88$

λ, Int	ν	Δν	m	mδ
5875 960 (1)	17013 79	0 99	(2)	12209 10
†5875 618 (10)	17014 78			
4471 689 (1)	22356 66	1 06	(3)	6866 16
†4471 477 (6)	22357 72			
4026 358 (1)	24829 34	1 05	(4)	4393 49
†4026 189 (5)	24830 39			
3819 753 (1)	26172 30	1 01	(5)	3050 57
†3819 606 (4)	26173 31			
3705 139 (1)	26981 90	0 98	(6)	2241 00
†3705 003 (3)	26982 88			
3634 37 (1)	27507 27	0 99	(7)	1715 62
3634 24 (2)	27508 26			
3587 42 (1)	27867 26	1 09	(8)	1355 53
3587 28 (2)	27868 35			
3554 57 (1)	28124 79	1 02	(9)	1098 07
3554 44 (1)	28125 81			
3530 50 (1)	28316 53		(10)	907 35
3512 50 (1)	28461 64		(11)	762 24
3498 63 (1)	28574 47		(12)	649 41
3487 72 (1)	28663 85		(13)	560 03
3478 95 (1)	28736 11		(14)	487 77
3471 78 (1)	28795 45		(15)	428 43
3465 89 (1)	28844 39		(16)	379 49
3461 2 ? (1)	28883 4		(17)	340 5
3456 7 (1)	28921 0		(18)	302 9

Fundamental $2\delta - m\varphi$
$2\delta = 12209\ 10$

λ, Int	ν	Δν	m	mφ
18684 2 (3)	5350 71		(3)	6858 39
12784 6 (1)	7819 83		(4)	4389 21

* Measures in I A (Paschen) λ10830 is the chief component

† Interferometer measures, Bureau of Standards, Washington

HELIUM, DOUBLET SYSTEM—*Continued*

COMBINATIONS

λ obs		ν calc
17002 55	5879 87	$2\pi_1-3\delta=5879\ 92$
	λ calc	
*3809 05	3809 08	$1\sigma-2\delta=26245\ 61$
*3166	3164 79	$1\sigma-3\delta=31588\ 55$
*2936	2935 03	$1\sigma-4\delta=34061\ 22$
*2824	2823 70	$1\sigma-5\delta=35404\ 14$
*2761	2760 57	$1\sigma-6\delta=36213\ 71$
*2722	2721 09	$1\sigma-7\delta=36739\ 09$
‡6059 8	6067 09	$1\pi_1-2\pi=16477\ 80$
‡4518 59	4517 43	$1\pi_1-3\pi=22130\ 29$
‡4045 87	4045 16	$1\pi_1-4\pi=24713\ 92$
‡3829 85	3829 42	$1\pi_1-5\pi=26106\ 22$
‡3711 15	3710 85	$1\pi_1-6\pi=26940\ 57$
‡3636 75	3637 96	$1\pi_1-7\pi=27480\ 09$

λ obs	λ calc	ν calc
‡ 3586 55	3589 85	$1\pi_1-8\pi=27848\ 38$
.	4275 81	$1\sigma-2\sigma=23380\ 84$
	3283 97	$1\sigma-3\sigma=30442\ 18$
†2986	2985 00	$1\sigma-4\sigma=33491\ 08$
†2851	2849 77	$1\sigma-5\sigma=35080\ 29$
†2777	2776 00	$1\sigma-6\sigma=36012\ 42$
†2732	2731 04	$1\sigma-7\sigma=36605\ 31$

* Stark's " diffuse principal " series, λ 3809 previously observed by Paschen
† Stark's ' sharp principal " series
‡ Stark's " near sharp " (fastscharfe) series, measures by Liebert Koch's " third subordinate " series

HELIUM, SINGLET SYSTEM

PRINCIPAL $1S-mP$
$1S=32032\ 51$

λ, Int	ν	m	mP
20582 04 (20)	4857 34	(1)	27175 17
† 5015 675 (6)	19931 95	(2)	12100 56
† 3964 727 (4)	25215 30	(3)	6817 21
† 3613 641 (3)	27665 06	(4)	4367 45
3447 594 (2)	28997 46	(5)	3035 05
3354 52 (1)	29801 99	(6)	2230 52
3296 76 (1)	30324 11	(7)	1708 40
3258 30 (1)	30682 04	(8)	1350 47
3231 20 (1)	30939 35	(9)	1093 16
3211 50 (1)	31129 13	(10)	903 38
3196 68 (1)	31273 45	(11)	759 06
		(12)	
3176 5? (1)	31472 4	(13)	560 1

SHARP $1P-mS$
$1P=27175\ 17$

λ, Int	ν	m	mS
—20582 04 (20)	—4857 34	(1)	32032 51
† 7281 349 (3)	13729 94	(2)	13445 23
† 5047 736 (2)	19805 35	(3)	7369 82
† 4437 549 (1)	22528 65	(4)	4646 52
4168 97 (1)	23980 00	(5)	3195 17
4023 99 (1)	24843 96	(6)	2331 21
3935 91 (1)	25399 92	(7)	1775 25
3878 18 (1)	25778 02	(8)	1397 15
3838 09 (1)	26047 26	(9)	1127 91
		(10)	930 15
3787 49 (1)	26395 24	(11)	779 93
3770 57 (1)	26513 69	(12)	661 48

FUNDAMENTAL $2D-mF$
$2D=12205\ 1$

λ, Int	ν	m	mF
18693 4 (2)	5348 0	(3)	6857 1
12792 2 (1)	7815 1	(4)	4390 0

† Interferometer measures, Bureau of Standards, Washington

DIFFUSE $1P-mD$
$1P=27175\ 17$

λ, Int	ν	m	mD
† 6678 149 (6)	14970 08	(2)	12205 09
† 4921 929 (4)	20311 57	(3)	6863 60
† 4387 928 (3)	22783 41	(4)	4391 76
4143 77 (2)	24125 84	(5)	3049 33
4009 27 (1)	24935 17	(6)	2240 00
3926 53 (1)	25460 59	(7)	1714 58
3871 80 (1)	25820 49	(8)	1354 68
3833 56 (1)	26078 04	(9)	1097 13
3805 75 (1)	26268 60	(10)	906 57
3784 88 (1)	26413 44	(11)	761 73
3768 80 (1)	26526 14	(12)	649 03
3756 09 (1)	26615 86	(13)	559 29

COMBINATIONS

λ	ν	ν calc
19090 58	5236 78	$2P-3D=5236\ 96$
λ obs	λ calc	
§ 6635	6631 84	$1P-2P=15074\ 61$
§ 4910 6	4910 61	$1P-3P=20357\ 96$
§ 4384 3	4383 25	$1P-4P=22807\ 72$
§ 4143 2	4141 32	$1P-5P=24140\ 12$
‡	5378 59	$1S-2S=18587\ 28$
‡	4053 56	$1S-3S=24662\ 69$
‡	3650 46	$1S-4S=27385\ 99$
‡ 3468	3466 74	$1S-5S=28837\ 34$
* 5043	5042 15	$1S-2D=19827\ 42$
‖ 3974	3972 04	$1S-3D=25168\ 91$
‖ 3618	3616 82	$1S-4D=27640\ 75$
‖ 3450	3449 29	$1S-5D=28983\ 18$
‖ 3356	3355 59	$1S-6D=29792\ 51$

* Merton, Proc Roy Soc, A **98**, 258 (1920).
‡ Stark's " sharp-principal " series
§ Observed by Merton, Stark, and Liebert
‖ Stark's " diffuse-principal " series

$m_1=3$ gives a strong series of which $\lambda 4686$ is the first member, and of which seven lines were observed, $m_1=4$ gives a fainter series with several lines in the visible spectrum, including the "Pickering lines", and $m_1=2$ gives a series in the Schumann region, of which two members have been observed by Lyman * There was at first some confusion as to the origin of these lines, but they may now be certainly attributed to ionised helium (p 62)

The fine structure of these lines has been studied by Paschen † Wave-lengths of the lines have been determined by Fowler, Evans,‡ and Paschen, as in the following table The values of Fowler and Evans have been corrected to the international scale, and those of Paschen are for the chief components of the complex lines observed by him Paschen's values are entitled to greatest weight

Fowler	Paschen	Fowler	Evans	Paschen	Lyman
4685 81	4685 808		6560 21	6560 130	
3203 17	3203 165	5410 29	5411 67	5411 551	1640 2
2733 24	2733 345			4859 342	1215 1
2511 22	2511 249	4541 13	4541 72	4541 612	
2385 39	2385 440		4339 81	4338 694	
2306 12	2306 215	4200 14	4199 79	4199 857	
2252 81				4100 049	

The values tabulated below have been calculated from the general formula, m being given integral values, and the constant $4N'$ having been calculated from the observed line 4685 81.

He$^+$ (Calculated Values).

"4686" Series

$$\nu=4\times 109723\ 22\left(\frac{1}{3^2}-\frac{1}{m^2}\right)$$

Limit $=A=48765\ 87$

$\lambda, I\ A$ (air)	ν	m	$A-\nu$
4685 81	21335 07	(4)	27430 80
3203 16	31210 16	(5)	17555 71
2733 34	36574 40	(6)	12191 47
2511 25	39808 87	(7)	8957 00
2385 46	41908 17	(8)	6857 70
2306 18	43347 44	(9)	5418 43
2252 72	44376 94	(10)	4388 93

"Lyman" Series

$$\nu=4\times 109723\ 22\left(\frac{1}{2^2}-\frac{1}{m^2}\right)$$

Limit $=109723\ 22$

$\lambda, I\ A$ vac	ν	m	$A-\nu$
1640 49	60957 35	(3)	48765 87
1215 18	82292 42	(4)	27430 80
1084 98	92167 51	(5)	17555 71
1025 31	97531 75	(6)	12191 47

"Pickering" Series *

$$\nu=4\times 109723\ 22\left(\frac{1}{4^2}-\frac{1}{m^2}\right)$$

Limit $=27430\ 80$

$\lambda, I\ A$ (air)	ν	m	$A-\nu$
10123 72	9875 09	(5)	17555 71
6560 16	15239 33	(6)	12191 47
5411 57	18473 80	(7)	8957 00
4859 36	20573 10	(8)	6857 70
4541 63	22012 37	(9)	5418 43
4338 71	23041 87	(10)	4388 93
4199 87	23803 59	(11)	3627 21
4100 08	24382 93	(12)	3047 87
4025 64	24833 80	(13)	2597 00
3968 47	25191 75	(14)	2239 25
3923 51	25480 17	(15)	1950 63
3887 47	25716 38	(16)	1714 42
3858 10	912 14	(17)	1518 66
3833 83	26076 19	(18)	1354 61
3813 53	215 03	(19)	1215 77
3796 36	333 57	(20)	1097 23
3781 71	435 58	(21)	995 22

* The original "Pickering" or "ζ Puppis" series included only alternate lines, beginning with 5411

* Nature, **104**, 314, 565 (1919)
† Ann d Phys , **50**, 901 (1916)
‡ Phil Mag , **29**, 284 (1915)

CHAPTER XII

GROUP Ia—THE ALKALI METALS

The chief series in the arc spectra of the alkali metals consist of doublets, the separations of which increase with the atomic weight There is also a general displacement of corresponding series in the different elements towards the red as the atomic weight increases Lines of the principal series are easily reversed and were traced towards their limits by Bevan* in his experiments on the absorption of the metallic vapours.

The allotment of the lines to the respective series is essentially as given by Dunz in his Tübingen dissertation In the principal series, the first pair appears with + sign in all the metals of the group, and the limits of the sharp and diffuse series consequently lie on the red side of the limits of the respective principal series The fundamental series lie still further to the red

The numeration of the diffuse series, following Rydberg, is based upon potassium, in which case the sharp and diffuse series are nearly coincident and the adjacent members have been assigned the same numbers There are then no lines with order-number less than 2 in the diffuse series, negative members corresponding to the order-number 1 not having been recorded

In the Rydberg formulæ for the principal series, μ is >1 except in the case of lithium , in the sharp and diffuse series μ is always <1 In the fundamental series the order-numbers have been chosen so as to make μ nearly unity

References to sources of data are given in connection with each element, but to avoid repetition it may be stated that the observations of Meggers† and Meissner‡ in the red have been utilised as far as possible

Enhanced lines have been observed in each of the elements except lithium, but no series have yet been identified

LITHIUM.

Li At wt =7 0 , At No =3

The arc spectrum of lithium is characterised by well-marked series, of which the principal has the first line in the red and the other members in the ultra-violet, whilst the brighter parts of the subordinate series are in the visible region, and the fundamental series in the infra-red The system consists of close doublets, as in the other alkali metals , but in the ordinary arc they are very diffuse, so that the components are not separated except in the case of the first principal line In vacuum tubes, however, five of the lines have been resolved into their components by N A Kent,§ who made use of a powerful echelon grating Kent's results are as follows —

λ	Δλ	$\Delta\nu$	Series
8126	0 225*A*	0 340	σ
6708	0 151	0 336	π
6103	0 115	0 309	δ
4972	0·084	0 339	σ
4603	0 070	0 328	δ

* Proc Roy Soc , A. **83**, 421 (1910) , **85**, 54 (1911) , **86**, 320 (1912)
† Scientific Papers, Bureau of Standards, Washington, No 312 (1918).
‡ Ann d Phys., **50**, 713 (1916)
§ Astrophys Jour , **40**, 337 (1914)

LITHIUM

PRINCIPAL $1\sigma - m\pi$
$1\sigma = 43486.3$

λ, Int	ν	m	$m\pi$
6707.85 (10*R*)	14903.8	(1)	28582.5
3232.61 (8*R*)	30925.9	(2)	12560.4
2741.31 (6*R*)	36468.1	(3)	7018.2
2562.50 (5*R*)	39012.7	(4)	4473.6
2475.29 (4*R*)	40387.1	(5)	3099.2
2425.68 (3*R*)	41213.0	(6)	2273.3
2394.48 (1*R*)	41750.0	(7)	1736.3
73.8	42113.6	(8)	1372.7
59.3	372.7	(9)	1113.6
48.4	569.1	(10)	917.2
40.4	714.6	(11)	771.7
34.2	828.0	(12)	658.3
28.9	925.6	(13)	560.7
25.1	995.6	(14)	490.7
21.8	43056.9	(15)	429.4
19.2	105.1	(16)	381.2
17.0	146.0	(17)	340.3
15.1	181.4	(18)	304.9
13.5	211.3	(19)	275.0
12.1	237.4	(20)	248.9
11.0	258.0	(21)	228.3
09.9	276.4	(22)	209.9
08.9	297.4	(23)	188.9
08.2	310.5	(24)	175.8
07.4	325.5	(25)	160.8
06.82	336.4	(26)	149.9
06.40	344.3	(27)	142.0
05.82	355.2	(28)	131.1
05.36	363.8	(29)	122.5
04.94	371.7	(30)	114.6
04.58	378.5	(31)	107.8
04.24	384.9	(32)	101.4
03.95	391.3	(33)	95.0
03.68	395.4	(34)	90.9
03.41	400.5	(35)	85.8
03.19	404.7	(36)	81.6
02.98	408.6	(37)	77.7
02.78	412.4	(38)	73.9
02.54	416.9	(39)	69.4
02.33	420.9	(40)	65.4
02.15	424.3	(41)	62.0

SHARP $1\pi - m\sigma$
$1\pi = 28582.5$

λ, Int	ν	m	$m\sigma$
—6707.85 (10*R*)	—14903.8	(1)	43486.3
8126.52 (10)	12302.0	(2)	16280.5
4971.93 (7*r*)	20107.3	(3)	8475.2
4273.28 (5*r*)	23394.7	(4)	5187.8
3985.79 (3*r*)	25082.1	(5)	3500.4
*3838.15 (1*r*)	26046.9	(6)	2535.6

* There is some doubt about these lines

DIFFUSE $1\pi - m\delta$
$1\pi = 28582.5$

λ, Int	ν	m	$m\delta$
6103.53 (10*R*)	16379.4	(2)	12203.1
4602.99 (9*R*)	21719.0	(3)	6863.5
4132.29 (8)	24192.9	(4)	4389.6
3915.0 (6)	25535.5	(5)	3047.0
3794.7 (5)	26345.1	(6)	2237.4
3718.7 (3)	26883.5	(7)	1699.0
3670.4 (1)	27237.3	(8)	1345.2

FUNDAMENTAL $2\delta - m\varphi$
$2\delta = 12203.1$

λ	ν	m	$m\varphi$
18697.0	5347.0	(3)	6856.1
12782.2	7821.3	(4)	4381.8

COMBINATION $1\pi - m\pi$
$1\pi = 28582.5$

λ	ν	m	ν calc
6240.1	16021.0	(2)	16022.1
4636.1	21563.9	(3)	21564.3
4148.0	24101.2	(4)	24108.9
*3921.65	25492.3	(5)	25483.3

COMBINATION $2\pi - m\sigma$
$2\pi = 12560.4$

λ	ν	m	ν calc
24467.0	4086.1	(3)	4085.2
13566.4	7369.5	(4)	7372.6

COMBINATION $2\pi - m\delta$
$2\pi = 12560.4$

λ	ν	m	ν calc
17551.6	5696.0	(3)	5696.9
12232.4	8172.8	(4)	8170.8

OTHER Li COMBINATIONS

λ	ν	ν calc
4601.4	21726.5	$1\pi - 3\varphi =$ 21726.4
19290	5182.6	$2\delta - 3\pi =$ 5184.9
26875.3	3719.9	$2\sigma - 2\pi =$ 3720.1
40475	2470.0	$3\delta - 4\delta =$ 2473.9
		$3\varphi - 4\varphi =$ 2474.3
7.436μ	1344.4	$4\delta - 5\delta =$ 1342.6

Unclassified

λ	ν
23990.8	4167

The variations in $\Delta\nu$ are believed to be real It seems probable that the σ and π pairs are equal, while the smaller values for the δ pairs are due to normal close satellites

Combinations are numerous, and in view of the uncertainties in the wave-lengths, the calculated are in satisfactory agreement with the observed positions The combinations entered as $3\delta-4\delta$ and $4\delta-5\delta$ were respectively given by Dunz as $4\,\Delta p-N/5^2$ $(=3\mathfrak{p}-N/5^2)$ and $N/5^2-N/6^2$

Lines 2-7 of the principal series are from observations by Huppers,* and 8-41 from Bevan The estimated possible error in Bevan's values is 0 3*A*, but the error in relative positions is probably much smaller Other lines are from Paschen, Kayser and Runge, and Saunders

The principal series is represented fairly well by the formula

$$\pi_1(m)=43486\ 3-N/(m+0\ 951125+0\ 007766/m)^2$$

he residuals being

m	1	2	3	4	5	6	10	15
$O-C$ ($\Delta\nu$)	0·0	0 0	−1 9	−2 9	−3 9	−4 2	−2 8	+1 6
m	20	25	30	35	40			
$O-C$ ($\Delta\nu$)	+1 0	+2 1	−0 1	−1 1	0 0			

Sodium

Na At wt =23 00, At No =11

The arc lines of sodium form a system of pairs, of which the well-known strong lines in the yellow are the first of the principal series Other members of the π series lie in the ultra-violet, but σ and δ are almost entirely in the visible spectrum The fundamental series lies in the red and infra-red

The principal series has been traced in the absorption spectrum as far as the 57th member by Wood and Fortrat,† who measured the positions of the lines on the international scale with great accuracy, the wave-lengths tabulated are as given by them, and have been re-reduced to wave-numbers in vacuo with the aid of the Washington tables The following formulæ have been calculated —

$$\pi_1(m)=41449\ 00-N/(m+1\ 148066-0\ 031200/m)^2$$

$$\pi_2(m)=41449\ 00-N/(m+1\ 147231-0\ 031108/m)^2$$

For π_1 the residuals are

m	1	2	3	4	5	6	7	10
$O-C(\Delta\nu)$	0 00	+1 43	0 00	−0 33	+0 08	−0 11	−0 26	−0 39
m	15	20	30	35	40	45	50	
$O-C(\Delta\nu)$	−0 38	+0 18	+0 22	−0 25	−0 10	−0 04	−0 01	
m	54	55	56	57				
$O-C(\Delta\nu)$	−0 01	−0 24	−0 81	−1 34				

It is clear that the simple formula does not accurately represent the series, although the residuals rarely exceed a few hundredths of an angstrom Hicks‡ has

* Zeit f. Wiss Phot, **13**, 46 (1914)
† Astrophys Jour, **43** 73 (1916)
‡ Astrophys Jour, **44**, 231 (1916)

Na Doublets

PRINCIPAL $1\sigma - m\pi$
$1\sigma = 41449\ 00$

λ, Int	ν	Δν	m	$m\pi_{1,2}$
5889 963 (10*R*)	16973 35	17 18	(1)	24475 65
95 930 (8*R*)	956 17			24492 83
3302 34 (8*R*)	30272 86	5 49	(2)	11176 14
02 94 (7*R*)	267 37			11181 63
2852 828 (6*R*)	35042 66	2 49	(3)	6406 34
53 031 (5*R*)	040·17			6408 83
2680 335 (5*R*)	37297 70	1 50	(4)	4151 30
80 443 (4*R*)	296 20			4152 80
2593 828	38541 54	1 47	(5)	2907 46
93 927	540 07			2908 93
2543 817	39299 20	0 89	(6)	2149 80
43 875	298 31			2150 69
2512 128	39794 92	1 31	(7)	1654 08
12 210	793 61			1655 31
2490 733	40136 72		(8)	1312 28
75 533	383 14		(9)	1065 86
64 397	565 60		(10)	883 40
55 915	705 69		(11)	743 31
49 393	814 08		(12)	634 92
44 195	900 87		(13)	548 13
40 046	970 41		(14)	478 59
36 627	41027 90		(15)	421 10
33 824	075 14		(16)	373 86
31 433	41115 53		(17)	333 47
29 428	149 46		(18)	299 54
27 705	178 67		(19)	270 33
26 217	41203 91		(20)	245 09
24 937	225 65			223 35
23 838	244 35			204 65
22 856	261 07			187 93
21 997	275 70			173 30
21 233	288 72		(25)	160 28
20 520	41300 88			149 12
19 922	11 07			137 93
19 380	20 34			128 66
18 893	28 67			120 33
454	36 17		(30)	112 83
062	42 86			106 14
17 695	49 11			99 89
362	54 83			94 17
058	60 03			88 97
16 779	64 81		(35)	84 19
518	69 27			79 73
271	73 50			75 50
046	77 35			71 65
15 838	80 91			68 09
651	84 12		(40)	64 88
474	87 15			61 85
305	90 05			58 95
147	92 75			56 25
006	95 16			53 84

PRINCIPAL $1\sigma - m\pi$ (*continued*)
$1\sigma = 41449\ 00$

λ, Int	ν	Δν	m	$m\pi_{1,2}$
2414 872	41397 46		(45)	51 54
746	9 61			49 39
627	41401 66			47 34
518	3 53			45 47
411	5 37			43 63
313	7 06		(50)	41 94
218	8 69			40 31
131	41410 19			38 81
050	1 57			37 43
13 971	2 93			36·07
910	3 97		(55)	35 03
873	4 61			34 39
837	5 22			33 78

SHARP $1\pi - m\sigma$
$1\pi_1 = 24475\ 65$, $1\pi_2 = 24492\ 83$

λ, Int	ν	Δν	m	$m\sigma$
—5889 963 (10*R*)	—16973 35	17 18	(1)	41449 00
— 95 930 (8*R*)	— 956 17			
11404 2	8766 34	16 79	(2)	15709 50
382 4	8783 13			
6160 725(8*r*)	16227 37	17 17	(3)	8248 28
54 214(8*r*)	244 54			
5153 645(6*n*)	19398 34	17 17	(4)	5077 31
49 090(5*n*)	415 51			
4751 891(4*n*)	21038 37	17 18	(5)	3437 28
48 016(3*n*)	055 55			
4545 218(4*n*)	21995 00	17 18	(6)	2480 65
41 671(3*n*)	22012 18			
4423 31 (4*n*)	22601 16	17 24	(7)	1874 49
19 94 (3)	618 40			
4344 8 (3)	23009 6	17 5	(8)	1466 0
41 5 (2)	027 1			
4290 6 (2)	23300 3	16 8	(9)	1175 5
87 5 (2)	317 1			
4252 4 (2)	23509 5	17 1	(10)	966 1
49 3	526 6			
4223 3	23671 4	16 8	(11)	804 4
20 3 (2)	688 2			
4201·0	23797 1	15 3	(12)	679 5
4198 3 (2)	812 4			

Na DOUBLETS—*Continued*

DIFFUSE $1\pi - m\delta$
$1\pi_1 = 24475\ 65$, $1\pi_2 = 24492\ 83$

λ, Int	ν	$\Delta\nu$	m	$m\delta$
8194 82 (10*R*)	12199 48	17 16	(2)	12276 18
83 30 (8*R*)	216 64			
5688 222 (10)	17575 30	17 17	(3)	6900 35
82 675 (8)	592 47			
4982 867 (6*r*)	20063 20	17 14	(4)	4412 47
78 608 (5*r*)	080 34			
4668 597 (4*r*)	21413 73	17 16	(5)	3061 92
64 858 (3*r*)	430 89			
4497 724 (2*n*)	22227 11	17 14	(6)	2248 56
94 266 (2*n*)	244 25			
4393 45	22754 77	17·19	(7)	1720 88
90 14	771 96			
4324 3	23118 7	16 6	(8)	1357 2
21 2	135 3			
4276 5	23377 0	17 0	(9)	1098 7
73 4	394 0			
4241 6	23569 3	15 6	(10)	907 1
38 8	584 9			
4215 6	23714 7	15 7	(11)	761 7
12 8	730 4			
4195 5	23828 3	16 4	(12)	647 7
92 6	844 7			
4180 0	23916 6	17 2	(13)	559 0
77 0	933 8			
4168	23985		(14)	491

FUNDAMENTAL, $2\delta - m\varphi$
$2\delta = 12276{\cdot}18$

λ	ν	$\Delta\nu$	m	$m\varphi$
18459 5	5415 81		(3)	6860 37
12677 6	7885 81		(4)	4390 37
		calc	(5)	3041 5

* The lines of this series are very faint, and the wave-lengths uncertain, this is often called the Lenard series
† Also $\delta_2(5)$

COMBINATION $1\pi - m\pi$ *

λ	ν	ν calc
5532 0	18071 6	$1\pi_1 - 3\pi_1 = 18069\ 3$
27 5	086 5	$1\pi_2 - 3\pi_2 = 18084\ 0$
4918 2	20327 0	$1\pi_1 - 4\pi_1 = 20324\ 4$
13 8	345 2	$1\pi_2 - 4\pi_2 = 20340\ 0$
4632 9	21578 7	$1\pi_1 - 5\pi_1 = 21568\ 2$
29 2	596 0	$1\pi_1 - 5\pi_2 = 21583\ 9$
4472 3	22353 6	$1\pi_1 - 6\pi_1 = 22325\ 9$
4372	22866	$1\pi_1 - 7\pi_1 = 22821\ 6$

OTHER Na COMBINATIONS

λ, Int	ν	ν calc
5675 70(3*v*)	17614 1	$1\pi_1 - 3\varphi = 17615\ 3$
70 18(3*v*)	631 2	$1\pi_2 - 3\varphi = 17631\ 5$
4975 9 (1*v*)	20091 3	$1\pi_1 - 4\varphi = 20085\ 3$
72 8 (1*v*)	103 8	$1\pi_2 - 4\varphi = 20102\ 5$
†4665 0	21430	$1\pi_1 - 5\varphi = 21434\ 1$
60 0	453	$1\pi_2 - 5\varphi = 21451\ 3$
22056 9	4532 5	$2\sigma - 2\pi_1 = 4533\ 4$
22084 2	4526 9	$2\sigma - 2\pi_2 = 4527\ 9$
3 418μ	2925	$2\pi_1 - 3\sigma = 2927\ 9$
5 430μ	1841	$3\sigma - 3\pi_1 = 1841\ 9$
9 048μ	1104 9	$2\delta - 2\pi_1 = 1100\ 0$
9 085μ	1100 5	$2\delta - 2\pi_2 = 1094\ 5$
23361 0	4279 5	$2\pi_2 - 3\delta = 4281\ 3$
23391 0	4273 9	$2\pi_1 - 3\delta = 4275\ 8$
50230	1990	$3\pi_1 - 4\delta = 1993\ 9$
40449	2471 6	$3\varphi - 4\varphi = 2470\ 0$
7 443μ	1343 2	$4\varphi - 5\varphi = 1348\ 9$
3427 1(1)	29170 8	$1\sigma - 2\delta = 29172\ 8$

Unclassified Lines of Na

λ	ν
7418 0	13477 0
7409 7	13492 1
7377 1	13551 7
7369 1	13566 4
3345 0	29886 8

drawn attention to the sudden increase of the residuals beyond $m=54$, and has suggested that the last three lines may not belong to the π series

The lines of σ from $m=3$ to $m=8$, and of δ from $m=3$ to $m=7$ are as determined by S Datta* from photographs of the spectrum of the sodium vapour lamp designed by Lord Rayleigh, in which the lines are very sharply defined $\delta(2)$ are from observations by Meggers, $\sigma(2)$ from Paschen, and the remainder are as obtained by Zickendraht† in the vacuum arc

The combinations are almost entirely as given by Dunz from the work of Paschen. $\lambda 40449$ is entered by Dunz as $3\mathfrak{p}-N/5^2$, and $\lambda 7\ 443\mu$ as $N/5^2-N/6^2$ Exner and Haschek's line at $\lambda 3427{\cdot}1$ has been included as a previously unrecognised combination.

Potassium

K At wt =39 10, At No =19

The arc lines of potassium form a doublet system similar to that of sodium The first and second π pairs, in the red and violet respectively, are developed in the Bunsen flame spectrum Bevan observed to the 24th member of the π series in the absorption spectrum, and the lines from $\pi(10)$ are as given by him The wavelengths of the principal pairs 2—4, of the σ pairs 4—10, of the δ pairs 4—10, and of the combination pair $1\sigma-2\delta$, are as determined by S Datta from observations with Lord Rayleigh's vapour lamp, in which the lines were much less diffuse than in air

The limits calculated from the σ pairs by Datta are 21963 06 and 22020 77, from which the limit of π becomes 35005 88 With this limit, the lines $\pi_1(1)$ and $\pi_1(2)$ lead to the formula

$$\pi_1(m)=35005\ 88-N/(m+1\ 296281-0\ 061661/m)^2$$

giving the following residuals —

m	1	2	3	4	5	10	15	20
$O-C(\Delta\nu)$	0 00	0 00	−2 80	+2 34	−0 76	−1 2	+4 0	0 0

m	21	22	23	24
$O-C(\Delta\nu)$	−0 6	+0 2	+0 8	−0 2

The presence of a satellite in $\delta(2)$ is strongly suggested by the combination $1\sigma-2\delta$, which was clearly resolved and accurately measured by Datta The less refrangible component of the combination is the stronger, and it would thus appear that the chief line in $\delta_1(2)$ is abnormally placed on the less refrangible side of the satellite The terms $2\delta'$ and 2δ entered in the table have been derived from the lines $(1\sigma-2\delta')-(1\sigma-1\pi_1)$ and $(1\sigma-2\delta)-(1\sigma-1\pi_1)$, thus eliminating errors of measurement of $\delta(2)$ The structure of $\delta(2)$ is probably as follows

	λ calc	ν calc	$\Delta\nu$	λ obsd
1st chief line	11771 5	8492 80	2 74	11771 73
Satellite	11767 9	8495 54	57 71	
2nd chief line	11688 3	8553 25		11689 76

The combination $1\sigma-2\delta,\delta'$ further suggests that the fundamental series should consist of pairs with $\Delta\nu=2\ 74$.

* Proc Roy Soc, A **99**, 69 (1921)
† Ann d Phys, **31**, 233 (1910).

K DOUBLETS

PRINCIPAL $1\sigma - m\pi$
$1\sigma = 35005\ 88$

λ, Int	ν	Δν	m	$m\pi_{1,2}$
7664 94 (10*R*)	13042 82	57 71	(1)	21963 06
99 01 (10*R*)	12985 11			22020 77
4044 140 (8*R*)	24720 18	18 69	(2)	10285 70
4047 201 (6*R*)	701 49			304 39
3446 722 (8*R*)	29004 70	8 15	(3)	6001 18
47 701 (6*R*)	28996 55			6009 33
3217 01 (6*R*)	31075 88	4 83	(4)	3930 00
17 50 (4*R*)	071·05			3934 83
3102 03 (4*R*)	32227 61	2 29	(5)	2778 27
02 25 (2*R*)	225 32			2780 56
3034 82 (4*R*)	32941 3		(6)	2064 6
2992 21 (2*R*)	33410 4		(7)	1595 5
63 24 (1*R*)	737 1		(8)	1268 8
42 7 (1*R*)	972 5		(9)	1033 4
27 9	34144 2		(10)	861 7
16 5	277 7			728 2
07 5	383 8			622 1
00 3	469 1			536 8
2894 5	538 1			467 8
89 6	596 7		(15)	409 2
85 8	642 4			363 5
82 8	678 4			327 5
80 2	709 7			296 2
77 8	738 6			267 3
75 7	764 0		(20)	241 9
74 0	784 6			221 3
72 4	803 9			202 0
71 0	820 9			185 0
69 9	834 2		(24)	171 7

SHARP $1\pi - m\sigma$
$1\pi_1 = 21963\ 06$, $1\pi_2 = 22020\ 77$

λ, Int	ν	Δν	m	mσ
—7664 94	—13042 82	57 71	(1)	35005 88
— 99 01	—12985 11			
12523 0	7983 16	56 94	(2)	13980 28
434 3	8040 10			
6938 98 (8)	14407 37	57 71	(3)	7555 69
11 30 (7)	465 08			
5802 16 (6*R*)	17230 20	57 77	(4)	4732 83
5782·77 (5*R*)	287 97			
5339 670 (4*R*)	18722 56	57 84	(5)	3240 44
23 228 (4*R*)	780 40			

SHARP $1\pi - m\sigma$—*continued*
$1\pi_1 = 21963\ 06$, $1\pi_2 = 22020\ 77$

λ, Int	ν	Δν	m	mσ
5099 180 (3*R*)	19605 54	57 74	(6)	2357 51
84 212 (2*R*)	663 28			
4956 043 (1*R*)	20171 61	57 63	(7)	1791 49
41 964 (1*R*)	229 24			
4863 61	20555 16	58 17	(8)	1407 7
49 88	613 33			
4800 16	20826 82	57 76	(9)	1136 2
4786 89	884 58			
4754 54	21026 70	57 27	(10)	936 6
41 62	083 97			

DIFFUSE $1\pi - m\delta$
$1\pi_1 = 21963\ 06$, $1\pi_2 = 22020\ 77$

λ	ν	Δν	m	mδ
*11771 73	8492 64	59 6	(2)	13467 52δ
689 76	8552 19			470 26δ
†6965 0 (1)	14353 6	60 0	(3)	7608 3
† 36 0 (1)	413 6			
5832 31 (7*R*)	17141 13	57 78	(4)	4821 89
12 71 (6*R*)	198 91			
5359 521 (5*R*)	18653 20	57 80	(5)	3309 81
42 974 (4*R*)	711 00			
5112 204 (3*R*)	19555 61	57 77	(6)	2407 42
5097 144 (2*R*)	613 38			
4965 038 (1*R*)	20135 23	57 85	(7)	1827 76
50 816 (1*R*)	193 08			
4869 70	20529 46	57 77	(8)	1433 57
56 03	587 23			
4805 19	20805 0	61 3	(9)	1156 3
4791 08	866 3			
4759 31	21005 6	60 8	(10)	955 9
45 58	066 4			

* The terms 2δ are calculated from the combination $1\sigma - 2\delta, \delta'$ (*see* text)

† Roughly measured from reproduction in the Paper by Meggers The lines are abnormally faint

K DOUBLETS—*Continued*

FUNDAMENTAL $2\delta - m\varphi$
$2\delta = 13470{\cdot}3$

λ	ν	Δν	m	mφ
15166 3	6591 8		(3)	6878 5
11027 1	9066 1		(4)	4404 2
9600 04	10413 8		(5)	3056 5
8905 44	11226 0		(6)	2244 3
8504 3	11755 5		(7)	1714 8

K COMBINATIONS

λ	ν	ν calc
4642 172 (2)	21535 62	$1\sigma - 2\delta =$ 21535 62
41 585 (1)	538 36	$1\sigma - 2\delta' =$ 538 36
27065 6	3693 7	$2\sigma - 2\pi_1 =$ 3694 6
27215 0	3673 5	$2\sigma - 2\pi_2 =$ 3675 9
6 431μ	1554 4	$3\sigma - 3\pi_1 =$ 1554 5
6 461μ	1547 3	$3\sigma - 3\pi_2 =$ 1546 4
36626 4	2729 5	$2\pi_1 - 3\sigma =$ 2730 0
36372 7	2748 6	$2\pi_2 - 3\sigma =$ 2748 7
37354 3	2676 5	$2\pi_1 - 3\delta =$ 2677 4
37075 6	2696 4	$2\pi_2 - 3\delta =$ 2696 1

K COMBINATIONS—*continued*

λ	ν	ν calc
8 510μ	1174 8	$3\pi_1 - 4\delta =$ 1179 3
8 452μ	1182 9	$3\pi_2 - 4\delta =$ 1187 4
31395	3184 5	$2\delta - 2\pi_1 =$ 3184 6
31596 8	3164 0	$2\delta - 2\pi_2 =$ 3165 9
6 203μ	1611 6	$3\delta - 3\pi_1 =$ 1607 1
6 236μ	1603 1	$3\delta - 3\pi_2 =$ 1599 0
7 426μ	1346 3	$4\varphi - 5\varphi =$ 1347 7
*3650	27390	$1\sigma - 3\delta =$ 27397 6
*3062	32649	$1\sigma - 6\sigma =$ 32648·4

Unclassified Lines of K

λ	ν
40115 5	2492 1
*4600	21733
*4120	24265
*3580	27925

* Approximate wave-lengths of faint lines observed by Datta

It should be noted that several of the calculated combinations agree less closely with the observed values than is shown in the works of Paschen and Dunz In order to secure better agreement, Paschen assumed a higher value for the wave-length of $\pi_2(2)$ than that given by Kayser and Runge, and he explained that unless such correction were made the discordances of the corresponding combinations were greater than the probable errors of his infra-red measurements Paschen's assumed wave-length has not been confirmed by Datta

The intensities are as given by Kayser and Runge, except for the pair at 4642

RUBIDIUM

Rb At wt =85 45, At No =37

The arc lines of rubidium form a pair system resembling those of sodium and potassium, but with wider separation The wave-lengths of the principal series from λ 3228 onwards have been taken from the list of absorption lines given by Bevan Other wave-lengths are by Meggers, Kayser and Runge, Paschen, and Randall

The satellites in δ would appear to be somewhat abnormal A satellite is clearly indicated in $\delta(3)$, and the smaller separations of other δ pairs also suggest the presence of satellites in the usual positions In $\delta(2)$, however, only two lines have been recorded, and these show the same separation as the σ pairs The real absence of a

Rb Doublets

Principal $1\sigma - m\pi$, $1\sigma = 33689\ 1$					Diffuse $1\pi - m\delta$, $1\pi_1 = 20872\ 6$, $1\pi_2 = 21110\ 2$				
λ, Int	ν	Δν	*m*	$m\pi_{1,2}$	λ, Int	ν	Δν	*m*	$m\delta', \delta$
					15290 3	6538 3		(2)	14334 3
7800 29(10*R*)	12816 5	237 6	(1)	20872 6	——	——	237 7		——
7947 64 (8*R*)	578 9			21110 2	14754 0	6776 0			
4201 82 (8*R*)	23792 5	77 5	(2)	9896 6					
15 56 (7*R*)	715 0			9974 1	7759 61 (1)	12883 7	3 0	(3)	7988 9
					57 83 (8)	886 7			7985·9
3587 08 (5*R*)	27869 9	35 0	(3)	5819 2			237 6		
91 59	834 9			5854 2	7619 12 (8)	13121 3			
3348 72 (3*R*)	29853 6	19 3	(4)	3835 5					
50 89 (5*R*)	834 3			3854 8	——	——		(4)	5002 4
					6298 50(10)	15872 4			5000 2
3228 05	30969 5	10 3	(5)	2719 6					
29 13	959 2			2729 9	6206 48 (8)	16107 8			
3157 56	31660 9	5 6	(6)	2028 2					
58 12	655 3			2033 8	——	——		(5)	3409 6
					5724 19 (4*r*)	17464 9			3407 7
3112 83	32115 8		(7)	1573 3					
3082 27	434 3		(8)	1254 8	5647 96 (3*r*)	700 6			
60 50	664 9		(9)	1024 2					
44 21	839 8		(10)	849 3					
32 08	971 1		(11)	718 0	——	——		(6)	2468 2
22 60	33074 5		(12)	614 6	5431 62 (2*r*)	18405 6			2467 0
15 04	157 4		(13)	531 7					
08 91	225 0		(14)	464 1	5362 75 (2*r*)	642 0			
03 99	279 4		(15)	409 7					
2999 84	325 5		(16)	363 6					
96 39	363 8		(17)	325 3	——	——		(7)	1868 8
93 40	397 1		(18)	292 0	5260 3	19005 0			1867 6
91 00	423 9		(19)	265 2					
88 82	448 3		(20)	240 8	5195 7	241 4			
86 89	469 9		(21)	219 2					
85 33	487 4		(22)	201 7					
83 93	503·1		(23)	186 0	——	——		(8)	1464 6
82 56	518 5		(24)	170 6	5150 8	19409 1			1463 5
81 39	531 6		(25)	157 5					
80 40	542 8		(26)	146 3	5088 8	19645 6			
79 50	552 9		(27)	136 2					
78 69	562 0		(28)	127 1					
77 98	570 0		(29)	119 1	——	——		(9)	1182 7
77 27	33578 0		(30)	111 1	5075 8	19695 9			1176 7
					16 8	927 5			

Rb DOUBLETS—*Continued*

SHARP $1\pi-m\sigma$
$1\pi_1=20872\,6$, $1\pi_2=21110\,2$

λ, Int	ν	Δν	m	mσ
—7800 29(10*R*)	—12816 5	237 6	(1)	33689 1
—7947 64(8*R*)	— 578 9			
13066 7	7314 6	237 9	(2)	13557 9
237 0	7552 5			
7408 37 (10)	13494 5	237 6	(3)	7378 1
7280 22 (10)	732 1			
6159 84 (5)	16229 7	237 6	(4)	4642 9
6070 95 (2)	467 3			
5654 00	17681 7	237 0	(5)	3191 2
5579 2	918 7			
5391 0	18544 3	237 2	(6)	2328 5
22 9	781 5			
5233 8	19101 3		(7)	1773 8
5170 8	334 0			
5133 3	19475 2		(8)	1397 4

FUNDAMENTAL $2\delta-m\varphi$
$2\delta=14334\,3$

λ	ν	Δν	m	mφ
13443 7	7436 7		(3)	6897 6
10081 9	9916 1		(4)	4418 2
8873 6	11266 3		(5)	3068 0
8274 6	12081 9		(6)	2252 4

Rb COMBINATIONS

λ	ν	ν calc
27319 8	3659 4	$2\sigma-2\pi_1=$ 3661 3
27909 8	3582 0	$2\sigma-2\pi_2=$ 3583 8
38511 4	2595 9	$2\pi_2-3\sigma=$ 2596 0
6 436μ	1553 3	$3\sigma-3\pi_1=$ 1558 9
6 567μ	1522 3	$3\sigma-3\pi_2=$ 1523 9
22533 0	4436 7	$2\delta-2\pi_1=$ 4437 7
22936 7	4358 7	$2\delta-2\pi_2=$ 4360 2
5165 18	19355 0	$1\sigma-2\delta=$ 19354 8
52313 4	1911 1	$2\pi_1-3\delta=$ 1910 7
12924 1	7735 4	$2\sigma-3\pi_1=$ 7738 7
12986 6	7698 2	$2\sigma-3\pi_2=$ 7703 7
46190 1	2164 4	$3\delta-3\pi_1=$ 2166 7
4 637μ	2156 1	$3\delta-3\pi_1=$ 2166 7
4 696μ	2129 0	$3\delta-3\pi_2=$ 2131 7

Unclassified Lines of Rb

λ	ν
39866 9	2507 7
7 428μ	1345 9
7 269μ?	1375 3

Note —Meggers has found that a line observed by Eder and Valenta at λ7061 is due to barium, also that the line measured as λ8521 by Eder and λ8513 by Lehmann belongs to caesium

satellite in $\delta(2)$ is further suggested by the fact that only single lines have been recorded in the fundamental series, and also by the combination $1\sigma-2\delta$, which only appears as a single line

The general arrangement of the series is as given by Dunz, who adopted the combinations indicated by Paschen and Randall For the first two of the unclassified lines Dunz suggested the combinations $(3\varphi-N/5^2)$ and $(N/5^2-N/6^2)$, giving wave-numbers 2506 1 and 1340 5 respectively, in this connection it may be observed that $4\varphi-5\varphi=1350\,2$

The limit adopted for π is the mean of two closely accordant values deduced by Hicks and Johanson, corrected to the international scale From this and the first two lines the Hicks formula is

$$\pi_1(m)=33689\,1-N/(m+1\,365753-0\,073450/m)^2$$

This represents the lines very closely, as will appear from the following residuals

	1	2	3	4	5	6	10	15	20	25	30
$O-C(\Delta\nu$	0 0	0 0	+0 3	+0 1	−0 5	+0 1	+0 8	0 0	−0 5	+0 3	+0 4

CAESIUM

Cs At wt =132 8, At No =55.

The arc spectrum of caesium is generally similar to those of the other alkali metals, the main differences being that the characteristic pairs have a wider separation, and that satellites in the diffuse series are well-marked Observations have been very numerous, but the wave-length determinations in many cases still leave much to be desired; they could probably be improved by observations of the vacuum arc

The series are tabulated in accordance with Dunz, but the more recent data for the red lines given by Meggers and by Meissner have been incorporated Bevan's observations have been adopted for the principal series from the third pair onwards, and the wave-numbers have been re-calculated The wave-lengths for the fundamental series, and for the two unclassified pairs having the same separation, are from Meissner *

The limit adopted for the principal series is that given by Bevan, which, with $\pi_1(1)$ and $\pi_1(2)$, gives the formula

$$\pi_1(m) = 31401\,6 - N/(m + 1\,449446 - 0\,088216/m)^2$$

The residuals are

m	1	2	3	4	5	10	15	20	25	30	31
$O-C(\Delta\nu)$	0 0	0 0	−0 7	+0 1	−0 1	+1 5	−0 2	+0 2	−0 3	+1 3	+1 0

Bevan considered the possible errors in his wave-lengths to be about 0 2A, and the residuals are within this limit throughout

* New measures of lines in the red have since been published by Meissner (Ann d Phys. 65, 378, June 1921)

Cs Doublets

Principal $1\sigma - m\pi$ $1\sigma = 31404\ 6$					Diffuse $1\pi - m\delta$ $1\pi_1 = 19672\ 3$ $1\pi_2 = 20226\ 3$				
λ, Int	ν	Δν	m	$m\pi_{1\ 2}$	λ, Int	ν	Δν	m	$m\delta'$, δ
8521 12 (10*R*)	11732 3	554 0	(1)	19672 3	36127 0	2767 3	97 9	(2)	16905 0
8943 46 (10*R*)	178 3			20226 3	34892 0	2865 2			16807 1
							554 1		
4555 26 (8)	21946 5	181 4	(2)	9458 1	30100 0	3321 4			
93 16 (6)	765 4			9639 2					
3876 39 (6)	25789 9	80 6	(3)	5614 7	9208 40 (1)	10856 7	42 8	(3)	8815 6
88 65 (4)	709 3			5695 3	9172 23 (2)	899 5			8772 8
							554 0		
3611 52 (4)	27681 3	45 1	(4)	3723 3	8761 35 (5)	11410 7			
17 41 (2)	636 2			3768 4					
3476 88	28753 2	26 8	(5)	2651 4	6983 37 (5)	14315 8	20 9	(4)	5356 5
80 13	726 4			2678 2	73 17 (10)	336 7			5335 6
							554 5		
3398 14	29419 5	17 1	(6)	1985 1	6723 18 (10)	14869 8			
3400 00	402 4			2002 2					
3347 44	29865 0	11 4	(7)	1539 6	6217 27 (1)	16079 8	11 4	(5)	3592 7
48 72	853 6			1551 0	12 87 (8)	091 2			3581 1
							553 6		
3313 16	30174 0	8 0	(8)	1230 6	6010 33 (7)	16633 4			
14 04	166 0			1238 6					
3288 56	30399 8	5 3	(9)	1004 8	5847 64	17096 2	8 6	(6)	2575 7
89 13	394 5			1010 1	44 7	104 8			2507 5
							554 9		
3270 44	30568 1		(10)	836 0	5663 8	17651 1			
3256 66	697 5		(11)	707 1					
45 91	799 2		(12)	605 4					
37 47	879 5		(13)	525 1	——	——		(7)	1936 1
30 58	945 3		(14)	459 3	5635 22	17740 6			1931 7
25 00	998 8		(15)	405 8					
20 23	31044 7		(16)	359 9	5465 9	18290 2			
16 34	082 3		(17)	322 3					
12 91	115 5		(18)	289 1					
10 07	143 0		(19)	261 6	——	——		(8)	1508 3
07 67	166 3		(20)	238 3	5502 9	18167 3			1505 0
05 53	187 1		(21)	217 5					
03 69	205 0		(22)	199 6	5340 96	718 0			
02 02	221 3		(23)	183 3					
00 60	235 2		(24)	169 4					
3199 34	247 5		(25)	157 1	——	——		(9)	1208 6
98 14	259 2		(26)	145 4	5414 2	18464 8			1207 5
97 17	268 7		(27)	135 9					
96 09	279 2		(28)	125 4	5256 79	19017 7			
95 31	286 9		(29)	117 7					
94 48	295 0		(30)	109 6					
93 83	31301 4		(31)	103 2	——	——		(10)	996 4
					5350 8	18683 6			988 7
					5198 8	19229 9			
					——	——		(11)	828 5
					5303 8	18849 2			823 1
					5153 8	19397 8			

Cs DOUBLETS—*Continued*

SHARP 1π—$m\sigma$
$1\pi_1 = 19672\ 3$, $1\pi_2 = 20226\ 3$

λ, Int	ν	Δν	m	mσ
—8521 12	—11732 3	554 0	(1)	31404 6
—8943 46	—11178 3			
14694 8	6803 3	554 1	(2)	12868 9
13588 1	7357 4			
7944 11 (6)	12584 5	554 0	(3)	7087·8
7609 13 (5)	13138 5			
6586 94 (5)	15177 4	554 0	(4)	4494 9
6354 98 (4)	731 4			
6034 6	16566 5	554 7	(5)	3105 5
5839 11	17121 2			
5746 15	17398 1	554 5	(6)	2274 0
5568 7	952 6			
5574 2	17935	553	(7)	1738
5407 3	18488			

FUNDAMENTAL 2δ—$m\varphi$
$2\delta = 16807\ 1$, $2\delta' = 16905\ 0$.

λ, Int	ν	Δν	m	mφ
10124 1	9874 8	97 2	(3)	6932 6
025 4	9972 0			
8079 24(8r)	12374 0	97 8	(4)	4433 1
15 90(8r)	471 8			
7280 34(6r)	13731 9	97 8	(5)	3075 2
28 85(6r)	829 7			
6871 10(4n)	14549 7	98 0	(6)	2257 4
25 11(4n)	647 7			
6628 78	15081 6	97 7	(7)	1725 5
(6586 07) *	179 3			
6472 9	15444 7	98 2	(8)	1362 3
32 0	542 9			
6366 2	15703 5	98 0	(9)	1103 6
26 8	801 5			
6289 2	15896 0	96 8	(10)	911 6
51 1	992 8			
6232 2	16041 3		(11)	765 8

Unclassified Lines of Cs

λ, Int	ν	Δν
8053 35 (2v)	12413 8	97 3
7990 68 (2v)	511 1	
7270 70 (4v)	13750 1	97 1
7219 70 (4v)	847 2	
7 425μ	1346 4	
7 111μ?	1405 9	
6 931μ	1442 4	
39398 5	2537 5	
5209 (1)	19192	

Cs COMBINATIONS

λ	ν	ν calc
29318 3	3409 9	$2\sigma - 2\pi_1 = 3410\ 8$
30962 9	3228 8	$2\sigma - 2\pi_2 = 3229\ 7$
42202 3	2368 9	$2\pi_1 - 3\sigma = 2370\ 3$
39180 1	2551 6	$2\pi_2 - 3\sigma = 2551\ 4$
6 807μ	1468 6	$3\sigma - 3\pi_1 = 1473\ 1$
7 193μ	1390 2	$3\sigma - 3\pi_2 = 1392\ 5$
13605 2	7347 8	$2\delta - 2\pi_1 = 7349\ 0$
13761 2	7264 9	$2\delta' - 2\pi_2 = 7265\ 8$

* Calculated λ, line obscured by $\sigma(4)$

CHAPTER XIII.

GROUP Ib —COPPER, SILVER AND GOLD

These elements, like the alkali metals which form the first branch of Group I, yield spectra containing doublets The separations of the pairs, however, are greater in proportion to the atomic weights than in the first sub-group Thus silver with atomic weight 108, gives a doublet separation of 920, while caesium with atomic weight 133 gives a separation of 554. In these elements the typical series are not at all well developed, and there are many lines which remain unclassified The chief lines of copper and silver were classified by Kayser and Runge, and by Rydberg, and several combinations have since been noted by Dunz As in the spectra of the alkali metals, the first principal pair occurs with positive sign in the principal series

Extensive discussions of the three spectra in relation to the "oun" have been given by Hicks * With the aid of the theories of linkages and summation series which he has developed, Hicks has sought to associate a large number of lines with those belonging to the typical series Some of the individual illustrations, as Hicks acknowledges, are doubtless merely numerical coincidences It is largely by the indiscriminate association of spark with arc lines that his results have been obtained, and this is in direct opposition to our knowledge of the spark spectra of other elements in which series are well developed

Among the more recent observations of the spark spectra of the three elements are those by Eder,† covering the region $\lambda 2080 - \lambda 1855$

COPPER

Cu At wt =63 56, At No =29

Measures of the arc spectrum of copper have been made by Kayser and Runge and others, and more recently, in Kayser's laboratory, by Huppers‡ and by Hasbach,§ who give wave-lengths on the international scale Wave-lengths on the new scale have also been given by Meggers in the region $\lambda 8683 - \lambda 6415$

The lines are very numerous, and only a small percentage has been identified as representing the typical series or their combinations As shown by Rydberg,‖ however, there are many triplets and pairs having approximately constant differences of wave-number, but these have no obvious relation to the separations in the main series

The principal series of doublets is apparently represented by a characteristic strong pair in the near ultra-violet, showing appropriate Zeeman patterns, but there is no very convincing representation of the second or succeeding pairs The position of the second pair was calculated by Randall¶ as 2025 73, 2024 42 (Rowland scale), but Kayser and Runge observed only one line, at 2025 08(2*R*) Two lines in this region have since been photographed by Rubies, and D. M. Catalán** has suggested

* Phil Mag, Cu **39**, 457, Ag **38**, 301, Au **38**, 1 (1919).
† Zeit f Wiss Phot, **14**, 135 (1914)
‡ Zeit f Wiss Phot, **13**, 59
§ *Ibid* 399 (1914).
‖ Astrophys Jour, **6**, 239 (1897)
¶ Astrophys Jour, **34**, 1 (1911)
** An Soc Esp Fis y Quim, **15**, 432 (1917).

that they may correspond with the principal pair The wave-lengths are 2025 1, 2024 11, giving wave-numbers 49364 7, 49389 8, and a separation of 25·1 The probable combinations involving the term 2π, however, suggest a separation of 33, and it is doubtful whether the second pair is really represented in the spectrum In any case, there would seem to be an unusually rapid fall in intensity in the principal series

The series are here tabulated as in the memoir of Dunz, except that Hasbach's wave-lengths have been substituted and the wave-numbers re-calculated, the calculated $\pi(2)$ lines have also been slightly modified The meaning of the term "x" is not clear, but it may be noted that its value approximates to $N/(1\ 5)^2$

By extrapolation from the terms 2δ, $2\delta'$, Hicks has calculated the terms 1δ and $1\delta'$ as 28382 9 and 28410 0, and has suggested that the true fundamental series has these wave-numbers for limits By extrapolation from $3\varphi(=6880)$ he similarly found 12257 1 as the value of a possible term 2φ, terms for higher orders were also calculated, and he was thus able to compute the whole series from $m=2$ to $m=10$ The actual representatives suggested for this series, however, include two spark lines and one "displaced" line, and in four instances only one component is given It seems probable, therefore, that the terms 1δ have no real existence, and that the first pair of the fundamental series is represented by the tabulated infra-red lines observed by Randall

The constant difference lines to which attention was directed by Rydberg are too numerous for reproduction here, but it may be noted that they comprise —

6 triplets	with	$\Delta\nu$	129 5, 50 6
6 pairs	,,	,,	129 5
10 pairs	,,	,,	50 6
7 triplets	,,	,,	680,212
5 pairs	,,	,,	680
8 pairs	,,	,,	212

Some of the lines are used more than once in forming the combinations

A consideration of these pairs and triplets, using the probably more accurate values of Hasbach, suggests that some of the supposed constant differences are merely approximate numerical coincidences, though a majority may be sufficiently exact to be significant

Huppers has also attempted to identify constant-difference pairs, and has suggested a considerable number of pairs with separations averaging about 248, 79, 50 and 16 Most of these, however, are far from exact, and as spark lines have also been introduced, the results do not seem entitled to much weight The whole question is worthy of further investigation

There are numerous other lines which do not appear either in the regular series or in the constant difference groups

The spark spectrum of copper shows a multitude of lines, but regular series have not been traced It may be remarked that the Cu and Cu^+ lines are perhaps but imperfectly distinguishable in the existing tables, as enhanced lines occur quite prominently in the arc if observed near the poles

The spark spectrum in the Schumann region has been observed by Handke,* and the vacuum-arc spectrum by McLennan †

* Quoted in Lyman's book, and by McLennan

† Proc Roy Soc, A **98**, 105 (1920).

Cu Doublets

Principal $1\sigma - m\pi$
$1\sigma = 62308\ 0$

λ, Int	ν	$\Delta\nu$	m	$m\pi_{1,2}$
3247 55(10*R*)	30783 6	248 4	(1)	31524 4
73 97(10*R*)	535 2			772 8
‡[2024 33]	[49383 0]	32 7	(2)	[12925 0]
‡[2025 67]	[350 3]			[957 7]

Fundamental $2\delta - m\varphi$
$2\delta = 12365\ 9$, $2\delta' = 12372\ 8$

λ	ν	$\Delta\nu$	m	$m\varphi$
18229 5	5484 1		(3)	6880 0
194 7	94 6			
			(4)	[4400 0]
			(5)	[3656 0]

Sharp $1\pi - m\sigma$
$1\pi_1 = 31524\ 4$, $1\pi_2 = 31772\ 8$

λ Int	ν	$\Delta\nu$	m	$m\sigma$
—3247 55	—30783 6	248 4	(1)	62308 0
— 73 97	— 535 2			
8092 76 (10)	12353 3	248 5	(2)	19171 1
7933 19 (10)	601 8			
4530 84 (6*r*)	22064 8	248 7	(3)	9459 5
4480 38 (6*r*)	313 5			
3861 75 (3*n*)	25887 7	248 4	(4)	5636 7
25 05 (3)	26136 1			

Diffuse $1\pi - m\delta$
$1\pi_1 = 31524\ 4$, $1\pi_2 = 31772\ 8$

λ, Int	ν	$\Delta\nu$	m	$m\delta', \delta$
5220 04 (6)	19151 6	6 9	(2)	12372 8
18 17 (10)	158 5	248 3		365 9
5153 23 (8*n*)	19399 9			
4063 30 (4*n*)	24603 6	3 7	(3)	6920 8
62 69 (6*n*)	607 3	248 5		17 1
4022 67 (6*n*)	24852 1			
——	——		(4)	4415 5
3687 5 (3*n*)	27111 0			13 4
3654 3 (3*n*)	27357 3			

Cu Combinations

λ, Int	ν	ν calc
16008 5	6245 0	$2\sigma - 2\pi_1 = 6246\ 1$
16653 4	6003 2	$2\pi_1 - 3\delta' = 6004\ 2$
4056 7 (2*n*)	24643 7	$1\pi_1 - 3\varphi = 24644\ 4$
4015 8 (1*n*)	894 6	$1\pi_2 - 3\varphi = 24892\ 8$
3652 40 (1*n*)	27371 5	$1\pi_2 - 4\varphi = 27372\ 8$
3512 12 (4*n*)	28464 7	$1\pi_1 - 5\varphi = 28468\ 4$
2369 88 (6)	42183 4	$x - 3\varphi = 42182\ 6$
2238 43 (2*n*)	44660 3	$x - 4\varphi = 44662\ 6$
†5782 16 (8)	17289 8	$x - 1\pi_2 = 17289\ 8$
†5700 25 (6)	538 2	$x - 1\pi_1 = 17538\ 2$
*2768 89 (3)	36104 9	$x - 2\pi_2 = 36104\ 9$
66 39 (8)	137 6	$x - 2\pi_1 = 36137\ 6$
2723 95 (2)	36700 5	$x - \delta = 36696\ 7$

$x = 49062\ 6$

* Used in calculation of $2\pi_1$, $2\pi_2$
† Used in calculation of x
‡ Calc from combinations $x - 2\pi$

Silver

Ag At wt = 107 88, At No = 47

The arc spectrum of silver includes only a moderate number of lines, some of which are of great intensity Kayser and Runge's list contains several lines which are not given by Exner and Haschek as appearing in the arc. Further measures

Ag Doublets

Principal $1\sigma - m\pi$
$1\sigma = 61095\ 9$

λ, Int		$\Delta\nu$	m	$m\pi_{1\ 2}$
3280 66 (10*R*)	30472 9	920 6	(1)	30623 0
3382 86 (10*R*)	29552 3			31543 6
§[2061 19]	48500 1	202 9	(2)	12595 8§
§ 2069 85]	297 2			12798 7§

Sharp $1\pi - m\sigma$
$1\pi_1 = 30623\ 0$, $1\pi_2 = 31543\ 6$

λ, Int	ν	Δ	m	$m\sigma$
—3280 66 (10*R*)	—30472 9	920 6	(1)	61095 9
—3382 86 (10*R*)	—29552 3			
8273 73	12083 1	920 4	(2)	18540·0
7688 12	13003 5			
4668 52 (8*r*)	21414 1	920 4	(3)	9209 0
4476 12 (6*r*)	22334 5			
3981 72 (6*r*)	25107 7	918 8	(4)	5516 2
3841 15 (2*r*)	26026 5			
3709 96 (1*r*)	26946 8	921 8	(5)	3675 6
*3587 25	27868 6			
σ_1				
*3568 31	28016 5		(6)	2606 5
*3487 53	28665 5		(7)	1957 5
*3435 87	29096 4		(8)	1526 6

Ag Combinations $1\pi - 2\pi$

λ, Int	ν	calc
†5545 64 (4*r*)	18027 2	$1\pi_1 - 2\pi_1 = 18027\ 2$
†5276 2 (1*r*)	18947 8	$1\pi_2 - 2\pi_1 = 18947\ 8$
†5333 31 (2*r*)	18744 9	$1\pi_2 - 2\pi_2 = 18744\ 9$

Ag Combinations $1\pi - m\varphi$

λ	ν	ν calc
4212 60	23731 7	$1\pi_1 - 3\varphi = 23731\ 2$
4055 31	24652 1	$1\pi_1 - 3\varphi = 24651\ 8$
3810 71	26234 4	$1\pi_1 - 4\varphi = 26236\ 8$
3682 30	27149 3	$1\pi_2 - 4\varphi = 27157\ 4$
3681 6	154 1	

Ag Combinations $2\sigma - 2\pi$

λ	ν	ν calc
16819 5	5943 9	$2\sigma - 2\pi_1 = 5944\ 2$
17415 7	5740 4	$2\sigma - 2\pi_2 = 5741\ 3$

Diffuse $1\pi - m\delta$
$1\pi_1 = 30623\ 0$, $1\pi_2 = 31543\ 6$

λ, Int	ν	Δν	m	$m\delta'$, δ
5471 51 (6)	18271·4	20 3	(2)	12351 6
‡ 65 45(10*R*)	291 7	920 5		331 3
‡5209 08(10*R*)	19191 9			
4212 60	23731 7	10 6	(3)	6891 4
10 71 (8*R*)	742 3	920 4		6880 7
4055 31 (6R)	24652 1			
			(4)	4394 3
3810 71 (2*n*)	26234 4			4388 6
3682 30 (2*n*)	27149 3			
			(5)	3040 2
3623 85 (1*n*)	27587 1			3035 9
*3507 35	28503 4			
			(6)	2224 6
*3520 35	28398 2			
*3409 76	29319 2			
			(7)	1698 3
*3456 25	28924 8			
*3349 66	29845 2			
*3413 66	29285 7		(8)	1337 3

Fundamental $2\delta - m\varphi$
$2\delta = 12331\ 3$, $2\delta' = 12351\ 6$

λ	ν	Δ	m	$m\varphi$
18382 3	5438 6	22 1	(3)	6891 8
307·9	5460 7			
12551 0	7965 4		(4)	1386 2?

*Observations by Catalán
†Used in calculation of $2\pi_1$ and $2\pi_2$
‡Fabry & Perot's wave-lengths are 5465 489, 5209 081
§Calc from combinations $1\pi - 2\pi$ Catalán's observed λλ are 2061 7, 2070 3

on the new scale have been made by Kaspar,* and by Frings † Measures in the ultra-violet beyond λ2983 have also been given by Huppers‡, the suggested series in this region, however, are probably fictitious The majority of the lines are somewhat nebulous, and high precision in the measurements is scarcely to be expected

The series are here tabulated in accordance with the memoir by Dunz, chiefly using Kayser and Runge's wave-lengths, but they have been extended towards the violet as indicated by Catalán § The adopted limit has been calculated from the sharp series

The spark spectrum of silver is much more complex than the arc spectrum, but many of the lines are of low intensity No series have yet been traced Hicks,‖ however, has made an extensive investigation of the lines in connection with his theory of linkages New measures of the spark lines have been made by Frings, Wagner,¶ and Eder **

Gold

Au At wt =197 2, At No =79

Series have not yet been very clearly traced in the spectrum of gold Two pairs of lines of equal separation and appropriate to a doublet system of this element were noted by Rydberg, together with a possible diffuse pair and satellite The latter, however, are probably not significant An additional pair has since been found through Lehmann's observations†† in the extreme red, showing a line which pairs with one in the orange The discussion of the spectrum by Hicks also suggested further pairs, but spark lines are involved in some of them, and there is probably only one (4811, 4065) which is real

Measures of the arc spectrum on the international scale have been made in Kayser's laboratory by Quincke,‡‡ whose values have been adopted for the lines mentioned below, except for Lehmann's line 7509 The four most probable pairs are

λ, Int	ν	Δν
7509 5	13312 8	3813 4
5837 396 (4)	17126 19	
6278 179 (4)	15923 79	3815 55
5064 616 (2*n*)	19739 34	
4811 611 (4*n*)	20777 27	3815 58
4065 080 (6)	24592 85	
2427 978 (10*R*)	41174 02	3815 22
2675 953 (10*R*)	37358 78	

* Zeit f Wiss Phot, **10**, 53 (1912)
† *Ibid*, **15**, 165 (1915)
‡ Zeit f Wiss Phot, **13**, 51 (1914)
§ An Soc Esp Fis y Quim, **15**, 222 (1917).
‖ Phil Trans, A **217**, 374 (1918)
¶ Zeit f Wiss Phot, **10** (1912)
** Zeit f Wiss Phot, **13**, 20, and **14**, 137.
†† Ann d Phys, **39**, 75 (1912)
‡‡ Zeit. f Wiss Phot, **14**, 249 (1915)

The very strong pair in the ultra-violet has usually been regarded as the first of the principal series, analogous with those of Ag and Cu, but Hicks argues against this supposition on the ground that the wave-lengths are not in step with 3280, 3382 for Ag and 3247, 3274 for Cu. It may be remarked, however, that the first principal Li pair is similarly out of step with those of Na and K

The first pair in the list is assigned to the sharp series by Lehmann and Hicks, forming $\sigma_1(2)$ and $\sigma_2(2)$, the line 5837 gives a Zeeman resolution in accordance with this supposition The second pair, in association with a line $\lambda 5230\ 306(1n)$, or $\nu 19114\ 03$, is described by Hicks as an inverse set of the diffuse type The third pair is assigned to the sharp series by Hicks, who also places the limit for σ_1 at 29470 Assuming the fourth pair to be the first principal, the limit of the principal series would thus be 70664

The spark spectrum of gold comprises a very large number of lines, but typical series have not been identified

CHAPTER XIV.

GROUP IIA —THE ALKALINE EARTH METALS

Apart from beryllium, which requires further investigation in the region of short wave-lengths, the arc spectra of these elements include a triplet system and a system of singlets There are combinations in each system, and also a certain number of inter-combinations, of which $1S-1p_2$ is of considerable importance in adjusting the limits in the two systems so as to yield accurate combinations

In each of the triplet systems the limit of the principal series lies on the less refrangible side of the limits of the subordinate series, and the first principal line appears with negative sign in the principal series and with positive sign in the sharp series In the formulæ for the sharp series, Rydberg's μ has to be given a value >1 in order that $m=1$ may give the first line The diffuse series differ from those of the alkali metals in exhibiting lines corresponding to $m=1$ (except in the case of Mg) when μ is put <1 The numeration of the diffuse series also differs from that adopted in the alkalis, and is possibly not altogether satisfactory In the alkalis, lines of the diffuse series were assigned the same numbers as the lines of the sharp series to which they were nearest, but to do this in the alkaline earth metals would require either that the first diffuse triplet should be numbered zero, or that the first sharp and principal triplet should be given the order-number 2 That the actual first d triplets have been recorded is indicated by their connection with the f series

In the singlet systems, the component series are arranged in the same way as in lithium, and the chief difference lies in the appearance of lines corresponding to $m=1$ in the diffuse series, except in the case of magnesium

The enhanced lines form systems of pairs, having $4N$ for the series constant, and showing no simple relations to the arc series These are tabulated under the headings "ionised Mg" (Mg^+), &c In each case the arc is a sufficient stimulus to excite some of the enhanced lines quite strongly, but these lines are more especially developed in the spark (*see* Plate IV)

MAGNESIUM

Mg At wt =24 32 , At No =12

The infra-red lines are from observations by Paschen Of the remaining lines, most of the wave-lengths are from a paper by Fowler and Reynolds,* but a few are from measures by Lorenser and by Meggers In the case of the triplets the limits adopted for the subordinate series are as calculated by Fowler and Reynolds, corrected to the international scale

The less refrangible components of the triplets are represented approximately by the following formulæ —

$$s_1(m)=39760\,5-N/(m+1\,376546-0\,062064/m)^2$$
$$d_1(m)=39760\,5-N/(m+0\,832086-0\,008310/m)^2$$

* Proc Roy Soc , A **89**, 137 (1913).

Mg TRIPLETS

PRINCIPAL $1s—mp$
$1s = 20474\ 5$

λ, Int	ν	Δν	m	$mp_{1,2,3}$
—5183 67 (10)	—19286 0	40 9	(1)	39760 5
— 72 70 (9)	— 326 9	19 9		39801 4
-- 67 38 (8)	— 346 8			39821 3
15023 3	6654 5	4 1	(2)	13820 0
032 7	50 4			824 1
032 7	50 4			824 1
7657 5	13055 5		(3)	7419 0
6318 55	15822 6		(4)	4651 9
6319 08	821 3			4653 2
5782 10	17290 0		(5)	3184 5

SHARP $1p—ms$
$1p_1 = 39760\ 5$, $1p_2 = 39801\ 4$, $1p_3 = 39821\ 3$

λ, Int	ν	Δν	m	ms
5183 67 (10)	19286 0	40 9	(1)	20474 5
72 70 (9)	326 9	19 9		
67 38 (8)	346 8			
3336 69 (8)	29961 2	40 9	(2)	9799 3
32 14 (7)	30002 1	19 8		
29 91 (6)	021 9			
2942 10 (6)	33979 4	40 8	(3)	5781 3
38 56 (5)	34020 2	19 6		
36 88 (4)	039 8			
* [2781 33	35943 6	40 7	(4)	3817 0
* 78 17	984 3	19 9		
* 76 63]	36004 2			
2698 13 (5)	37051 7	40·6	(5)	2709 1
95 18 (4)	092 3	19 7		
93 75 (3)	112 0			
2649 02 (4)	37738 6	40 6	(6)	2022 1
46 17 (3)	779 2	19 9		
44 78 (2)	799 1			
2617 48 (3)	38193 3	41 3	(7)	1567 0
14 65 (2)	234 6			
2595 92 (2)	38510 4	40 6	(8)	1250 3
93 19 (1)	551 0			

* Calculated lines, the real lines being obscured.

DIFFUSE $1p—md$
$1p_1 = 39760\ 5$, $1p_2 = 39801\ 4$, $1p_3 = 39821\ 3$

λ, Int	ν	Δν	m	md
3838 29 (10)	26045 9	40 7	(2)	13714 7
32 31 (10)	086 6	20 1		
3229 36 (9)	106 7			
3096 91 (9)	32280 9	41 1	(3)	7479 5
92 97 (8)	322 0	19 8		
91 07 (6)	341 8			
2851 65 (8)	35057 1	39 6	(4)	4704 1
48 43 (7)	096 7	20 5		
46 77 (6)	117 2			
2736 53 (7)	36531 8	40 0	(5)	3229 3
33 54 (6)	571 8	19 8		
32 06 (5)	591 6			
2672 43 (6)	37408 1	40 2	(6)	2352 9
69 56 (5)	448 3	19 9		
68 14 (4)	468 2			
2632 88 (5)	37970 0	41 0	(7)	1790 3
30 04 (4)	38011 0	20 3		
28 63 (4)	031 3			
2606 64 (4)	38352 1	40 5	(8)	1408 5
03 89 (3)	392 6	20 5		
02 50 (2)	413 1			
2588 28 (3)	38624 2	40 9	(9)	1136 4
85 54 (2)	665 1	19 6		
84 23 (2)	684 7			
2574 93 (3)	38824 4	40 4	(10)	936 1
72 25 (2)	864 8	20 9		
70 87 (1)	885 7			
2564 91 (2)	38976 0	41 1	(11)	784 2
62 21 (1)	39017 1	20 4		
60 87 (1)	037 5			
2557 20 (2)	39093 5	39 6	(12)	667 6
54 61 (1)	133 1			
2551 13 (2)	39186 5	40 9	(13)	574 0
48 47 (1)	227 4			

COMBINATIONS

λ	ν	ν calc
15768 3	6340 2	$2p_1—3d = 6340\ 5$
15759 1	6343 9	$2p_2—3d = 6344\ 6$
10969 8	9113 5	$2p_1—4d = 9115\ 9$
10963 2	9119 1	$2p_2—4d = 9120\ 0$

Mg TRIPLETS—*Continued*

FUNDAMENTAL $2d—mf$ $2d=13714\ 7$

λ	ν	m	mf
14877'1	6719 9	(3)	6994 8
10812 9	9245 7	(4)	4469 0

COMBINATION $1p—mf$

λ	ν	ν calc
3051	32766	$1p_1—3f=32765\ 7$
2833	35288	$1p_1—4f=35291\ 5$
2729	36633	$1p_1—5f$

COMBINATION $1p—2p$

λ	ν	ν calc
3854 11	25939 0	$1p_1—2p_1=25940\ 5$
3848 09	979 6	$1p_2—2p_1=25981\ 4$
3844 97	26000 6	$1p_3—2p_1=26001\ 3$
3854 53	25936 2	$1p_1—2p_2=25936\ 4$
3848 78	974 9	$1p_2—2p_2=25977\ 3$

Mg SINGLETS

PRINCIPAL $1S—mP$ $1S=61672\ 1$

λ Int	ν	m	mP
2852 11 (10R)	35051 4	(1)	26620 7
2025 82	49346 6	(2)	12325 5
1828 1	54702	(3)	6970

SHARP $1P—mS$ $1P=26620\ 7$

λ, Int	ν	m	mS
—2852 11 (10R)	—35051 4	(1)	61672 1
11828 8	8451 7	(2)	18169 0
5711 09 (4)	17504 9	(3)	9115 8
4730 16 (2)	21135 0	(4)	5485 7
4354 36 (1)	22959 1	(5)	3661 6

COMBINATION $2S—mP$ $2S=18169\ 0$

λ	ν	ν calc
—11828 8	— 8451 7	$2S—1P=-8451\ 7$
*17108 1	5843 6	$2S—2P=\ 5843\ 5$
8928 97	11196 4	$2S—3P=\ 11199$

COMBINATION $1P—mP$

λ	ν	ν calc
4511 2	22160 9	$1P—4P$† $=22162\ 6$
4250 8	23518 4	$1P—5P\ =23528\ 3$
4106 6	24344 2	$1P—6P$† $=24351\ 5$
4018 1	24880 4	$1P—7P$† $=24885\ 2$

Mg INTER-COMBINATIONS

λ	ν	ν calc
‡4571 15 (4)	21870 7	$1S—1p_3=21870\ 7$
12083 2	8273 7	$2D—3f\ =\ 8274\ 1$
9257 9	10798 6	$2D—4f\ =10799\ 0$
3043 75	32844 7	$1p_3—3P=32850\ 8$
2768 47	36110 3	$1p_1—5D=36111\ 8$
2765 34	36151 2	$1p_2—5D=36152\ 7$

DIFFUSE $1P—mD$ $1P=26620\ 7$

λ, Int	ν	m	mD
8806 75 (8)	11351 8	(2)	15268 9
5528 42 (8r)	18083 3	(3)	8537 4
4703 00 (8r)	21257 1	(4)	5363 6
4351 91 (7r)	22972 0	(5)	3648 7
4167 39 (6r)	23989 1	(6)	2631 6
4057 63 (5r)	24638 0	(7)	1982 7
3986 79 (4r)	25075 8	(8)	1544 9
3938 43 (3r)	25383 7	(9)	1237 0
3904 02 (2r)	25607 4	(10)	1012 3
3878 58 (1)	25775 3	(11)	835 4
3859 24 (1)	25904 5	(12)	716 2

Unclassified Lines of Mg

λ, Int	ν
23991 3 (15)	4167 0
23977 1 (8)	4169 5
23963 6 (5)	4171 9
17073 1	5855 6
11054 2? (15)	9043 9
7800 4 (1)	12816 4
7779 9 (1)	12850 1
6332 26 (2)	15787 8
6021 70 (1)	16602 0
2782 98 (6)	35922 1
§ 81 52 (6)	941 0
79 84 (6)	962 7
§ 78 29 (6)	982 7
§ 76 76 (6)	36002 5

* Johanson includes this in the Rydberg series as $—1P+1D$, giving $1D=32464\ 3$

† These are terms calculated by Lorenser The lines were observed by Fowler, and are all faint and diffuse

‡ Used in calculation of $1S$ This line occurs in the flame spectrum and is strong in the electric furnace at low temperatures

§ These closely represent a (*s*) triplet, but other lines are probably involved

The residuals $O-C(\Delta\nu)$ are as follows —

m	1	2	3	4	5	6	7	8	9	10	11	12	13
s	0 0	0 0	−0 5	−0 8	−0 8	−0 6	−0 8	−0 5					
d		0 0	0 0	−2 0	−2 3	−1 7	−2 0	−2 0	−1 5	−1 2	−1 0	−0 8	−0 7

In the formula for s, μ has been put >1 so that $m=1$ gives a positive value, in accordance with the occurrence of the p series on the less refrangible side of s If μ were <1 the formula would suggest a p series in the ultra-violet, but this has not been observed

Direct calculation of the limit for the diffuse series of singlets gave 26619 2, and thence, by adding the wave-number of the first principal line, 61670 6 for the limit of the principal series The limits adopted, however, have been derived from the combination $1S-1p_2=21870\ 7$, which gives 61672 1 for $1S$, and thence 26620 7 for $1P$

The combinations have been taken from the works of Dunz and Lorenser Attention has already been drawn (p 37) to the difficulty of representing the singlet D series by a formula

Ionised Magnesium (Mg^+)

The enhanced lines of magnesium have been the subject of an extended investigation by Fowler * The spectrum is remarkable for the fact that some of the enhanced lines appear conspicuously in the ordinary arc in air while others associated with them in their series relations only appear in the spark, or in the equivalent conditions in an arc in vacuo (*see also* p 66) The lines which appear in the arc in air are $\lambda\lambda$ 2936, 2928, 2802, 2795, 2798, 2790, constituting three pairs with a separation in wave-number of 91 5 Two pairs of like separation have been observed in the spark by Lyman at 1753 6, 1750 9, and 1737 8, 1735 0, it is not certain that these appear under ordinary arc conditions

In the spark in air the majority of the arc lines are present, but the first three pairs above mentioned are strengthened, and there is an intense broad line at λ4481 (*see* Pl IV), together with feeble indications of other extremely nebulous lines, including one about λ3105 As observed in the arc in vacuo, λ4481 becomes well-defined, and many other lines appear which are probably so diffuse in the spark as to escape detection Among the additional lines are a number of doublets having a separation of 30 5, and two series of single lines Under the conditions of the vacuum arc, the line 4481 is revealed as the leader of a strong series which extends far into the ultra-violet, with high resolution, the first three members have been shown to be very close doublets, having the stronger components on the more refrangible sides, and a constant separation $\Delta\nu$ of 0 99 The other members of the series are too close for resolution with the grating This series is of the fundamental (φ) type

The doublets of separation 91 5, the first of which appears in the arc, as well as in the spark, have been arranged in principal (π), sharp (σ), and diffuse (δ) series Most of the members of the series lie in the Schumann region, outside the range of the observations at present available, their positions, however, can be calculated with considerable certainty from the data given by the parallel series of doublets having separation 30 5 The possible associated fundamental series, given by

* Phil Trans, A 214, 225 (1914)

$1\delta - m\varphi$ (where 1δ is about 110830 and 3φ about 27467), would lie in the Schumann region, and has not been recorded (*see also* p 66)

The doublets with separation 30 5* may be regarded as forming a secondary system, based upon the second member of the main principal series, which the calculations prove to have an identical separation The σ and δ series of this second system are well marked, but the π series has only been partially observed The "4481" series is the fundamental series of this secondary system The more refrangible (stronger) members of these pairs are closely represented by the formula

$$\varphi(m) = 49777\ 07 - \frac{4 \times 109678\ 3}{\left[m + 0\ 994112 + \frac{0\ 007190}{m}\right]^2}$$

in which the constants have been calculated from the first, second, and eighth lines The differences $O-C$, in wave-number, for the eight lines are 0 00,† −0 01,† −0 35, −0 32, −0 58, −0 17, −0 11, and 0 00 † Notwithstanding their small magnitude, the residuals are sufficiently systematic to show that the formula is not exact The largest residual is equivalent to 0 03*A* The unresolved lines have been regarded as consisting of two components, separated by 0 99, and since in the resolved lines the more refrangible components have about twice the intensity of the less refrangible, the observed wave-numbers have been increased by 0 33 for comparison with the formula As in most fundamental series, it will be noted that the value of μ approximates to unity The fact that this series consists of doublets indicates the presence of a satellite in the δ doublet 2798, 2791, with which it is connected The satellite has not been directly observed, but its presence is indicated by the wider separation of the chief lines as compared with the other doublets of the same system The arrangement is unusual, as the chief line is displaced to the red side of the presumed satellite, but this accords with the greater intensity of the *more* refrangible components of the 4481 series

A combination series $3\delta - m\varphi$ is well marked, and the calculated values do not differ greatly from the observed, though the differences are fairly systematic

The series $3\varphi - m\varphi$ is apparently represented, and is of special interest because the calculated values show a clearly systematic deviation from the observed The terms involved depend upon observations of great accuracy, and the combinations are independent of the adopted value of the limit of the 4481 series

The separation 14 1 of the third π pair re-appears in the combination $2\delta - 3\pi_{1,2}$

Formulæ for the individual series were given by Fowler, and served to justify the arrangement of the lines adopted in the accompanying table All the observed enhanced lines are included in the scheme In drawing up the table, the limits 49777 0 and 49776 0 have been adopted for the "4481" series, and all the other limits have been derived from these with the aid of observed lines, whether occurring in the main series or in combinations Thus, starting with $2\delta = 49777\ 0$, we have $1\pi_1 = 2\delta + \delta(2) = 49777\ 0 + 35729\ 44 = 85506\ 44$, and $1\sigma = 1\pi_1 + \pi_1(1) = 85506\ 44 + 35760\ 97 = 121267\ 41$

* These have sometimes been designated the "FP" (Fowler and Payn) doublets of magnesium

† Used in calculation of constants

Mg^+ Doublets

Principal $1\sigma - m\pi$

$1\sigma = 121267\ 41$

λ, Int	ν	Δν	m	$m\pi_{1,2}$
2795 523 (50)	35760 97	91 55	(1)	85506 44
2802 698 (50)	35669 42			597 99
1239 9*	80651 3	30 5	(2)	40616 1
1240 4*	80620 8			646 6
1026 0*	97469 0	14 1	(3)	23798 4
1026 1*	97454 9			812 5

Sharp $1\pi - m\sigma$

$1\pi_1 = 85506\ 44$ $1\pi_2 = 85597\ 99$

λ, Int	ν	Δν	m	$m\sigma$
—2795 523 (50)	—35760 97	91 55	(1)	121267 4
—2802 698 (50)	—35669 42			
2936 496 (35)	34044 25	91 49	(2)	51462 2
28 625 (35)	34135 74			
1753 6	57027	88	(3)	28481 2
50 9	57115			

Diffuse $1\pi - m\delta$

$1\pi_1 = 85506\ 44$, $1\pi_2 = 85597\ 99$

λ, Int	ν	Δν	m	$m\delta$, δ'
2797 989 (40)	35729 44	0 99	(2)	49777 0
†	35730 43	91 46		776 0
90 768 (40)	35821 90			
1737 8	57546	93	(3)	27960
35 0	57639			

Combination, σ Type $2\pi - m\sigma$

$2\pi_1 = 40616\ 1$, $2\pi_2 = 40646\ 6$

λ, Int	ν	Δν	m	$m\sigma$
*	12134 9	30 5	(3)	28481 2
*	12165 4			
4433 991 (8)	22546 74	30 5	(4)	18069 3
27 995 (7)	22577 27			
3553 51 (5)	28133 2	30 9	(5)	12482 7
49 61 (4)	28164 1			
3175 84 (2)	31478 6	30 3	(6)	9137 6
3172 79 (1)	31508 9			
2971 70 (1)	‡33640 9	30 4	(7)	6975 2
2969 02 (0)	33671 3		(8)	5500 8*

* Calculated lines or terms

† Probable satellite

‡ Not resolved, 49776 7 adopted for limit.

Combination, π Type $2\sigma - m\pi$

$2\sigma = 51462\ 2$

λ, Int	ν	Δν	m	$m\pi_{1,2}$
—2936 496 (35)	—34044 25	91 49	(1)	85506 45
—2928 625 (35)	—34135 74			597 94
9217 4*	10846 1	30 5	(2)	40616 1
43 4*	10815 6			646 6
3613 80 (4)	27663 82	14 07	(3)	23798 4
15 64 (3)	27649 75			812 5
2790 33*	35827 5	7 6	(4)	15636 7
90 92*	35819 9			644 3

Combination, δ Type $2\pi - m\delta$

$2\pi_1 = 40616\ 1$, $2\pi_2 = 40646\ 6$

λ, Int	ν	Δν	m	$m\delta$
*	—9130 4	30 5	(2)	49777 0
*	—9160 9			
7896 37	12660 6	30 9	(3)	27955 3
77 13	12691 5			
4390 585 (10)	22769 64	30 86	(4)	17846 3
84 643 (8)	22800 50			
3538 86 (6)	28249 6	30 5	(5)	12366 5
35 04 (5)	28280 1			
3168 98 (3)	31546 8	30 3	(6)	9069 4
65 94 (2)	31577 1			
2967 87 (1)	33684 4	30 5	(7)	6931 7
65 19 (0)	33714 9			
			(8)	5471 7*

Combination, φ Type $\left.\begin{matrix}2\delta \\ 2\delta'\end{matrix}\right\} - m\varphi$

$2\delta' = 49776\ 0$, $2\delta = 49777\ 0$

λ, Int	ν	Δν	m	$m\varphi$
4481 327 } (100)	22308 58	0 99	(3)	27467 4
81 129 }	22309 57			
3104 805 } (30)	32198 83	0 96	(4)	17577 2
04 713 }	32199 79			
2660 821 } (10)	37571 22	0 93	(5)	12204 8
60 755 }	37572 15			
‡2449 573 (6)	40811 08		(6)	8965 6
‡2329 58 (5)	42912 93		(7)	6863 8
‡2253 87 (4)	44354 35		(8)	5422 3
‡2202 68 (3)	45385 03		(9)	4391 7
‡2166 28 (2)	46147 60		(10)	3629 1
			(11)	3049 0*

Mg+ DOUBLETS—*Continued*

COMBINATION $3\delta - m\varphi$
$3\delta = 27955\ 3$

λ, Int	ν obs	ν calc	*m*
6340 67 (5)	15752 0	15750 5	(5)
5264 14 (5)	18991 2	18989 7	(6)
4739 59 (5)	21093 0	21091 5	(7)
4436 48 (5)	22534 1	22533 0	(8)
4242 47 (4)	23564 6	23563 6	(9)
4109 54 (3)	24326 8	24326 2	(10)
4013 80 (2)	24907 0	24906 3	(11)

COMBINATION $3\varphi - m\varphi$ (?)
$3\varphi = 27467\ 4$

λ, Int	ν obs	ν calc	*m*
6545 80 (5)	15272 8	15262 6	(5)
5401 05 (5)	18509 8	18501 8	(6)
4851 10 (5)	20608 2	20603 6	(7)
4534 26 (4)	22048 1	22045 1	(8)
4331 93 (3)	23078 0	23075 7	(9)
4193 44 (2)	23840 1	23838 3	(10)
4093 90 (1)	24419 7	24418 4	(11)

COMBINATION $2\delta - 3\pi_{1,2}$
$2\delta = 49776\ 7$

λ, Int	ν obs	ν calc	Δν
3850 40 (6)	25964 0	25964 2	14 6
3848 24 (7)	25978 6	25978 3	

CALCIUM

Ca At wt =40 07, At No =20

The arc spectrum of calcium includes a system of triplets and a system of singlets Lines of a doublet system also occur in the spectrum of the arc, but these belong to ionised calcium (Ca^+) and will be considered separately

Data relating to the arc lines have been collected and much extended by Saunders,* and the series are tabulated as given by him Many of the adopted measures were made by Crew and McCauley,† who used the vacuum arc, and others were made by A S King in the course of his work with the electric furnace Preliminary observations of the infra-red region were provided by H M Randall A valuable set of wave-lengths has also been given by Holtz ‡

The *p* series of triplets lies in the infra-red, and has only been partiallyrecorded, but the *s*, *d*, and *f* series are well marked in the visible and ultra-violet regions In the *d* series, the separations of the satellites from the chief lines show marked irregularities, the usual shrinkage continuing only to the fourth member, after which the separations increase, the satellites, however, show constant separations from the third line characteristic of the triplet, and it is therefore the chief components which are abnormally displaced Reference has already been made to the difficulty of representing the *d* series by formulæ (p 42) The separations in the *f* triplets show the usual correspondence with those of the satellites of the first *d* triplet There are indications that the triplets of the *f* series have satellites, as in the case of barium, but the lines are too close for measurement in any but the first.

The *P* series of singlets begins with the well-known flame line 4226A, and all the lines are easily reversed, except the second, which is abnormally faint This does not reverse, as is also the case with the corresponding lines in Sr and Ba, but

* Astrophys Jour, **52**, 265 (1920)
† Astrophys Jour, **39**, 29 (1914)
‡ Zeit Wiss. Phot, **12**, 201 (1913)

Ca TRIPLETS

PRINCIPAL $1s—mp$

$1s = 17765\ 1$

λ, Int	ν	Δν	m	$mp_{1\,2\,1}$
— 6162 18(9)	—16223 6	105 9		33988 7
— 6122 22(8)	— 329 5	52 2	(1)	34094 6
— 6102 72(8)	— 381 7			146 9
19856 3	5034 8	19 9		*12730 3
19935 2	5014 9		(2)	750 2
	†10987 3	7 8		6777 8
	† 979 5	4 0	(3)	85 6
	† 975 5			89 6
	†13422 4		(4)	4342 7

SHARP $1p—ms$

$1p_1 = 33988\ 7$ $1p_2 = 34094\ 6$ $1p_3 = 34146\ 9$

λ, Int	ν	Δν	m	ms
6162 18 (9)	16223 6	105 9		
22 22 (8)	329 5	52 2	(1)	17765 1
02 72 (8)	381 7			
3973 72 (4)	25158 4	105 9		
57 05 (5)	264 3	52 2	(2)	8830 3
48 90 (3)	316 5			
3487 61 (5)	28664 9	106 0		
74 77 (3)	770 9	52 1	(3)	5323 8
68 48 (2)	823 0			
3286 06 (3)	30423 1	105 8		
74 66 (2)	528 9	52 1	(4)	3565 6
69 09 (1)	581 0			
3180 52 (2)	31432 5	105 8		
69 85 (1)	538 3	52 1	(5)	2556 2
64 62 (1)	590 4			
3117 66 (1)	32066 3	105 9		
07 39 (1)	172 2	52 2	(6)	1922 4
02 36 (0)	224 4			
3076 99	32490 1	105 7		
67 01	595 6	52 7	(7)	1498 6
62 05	648 5			
3049 01	32788 2	105 8		
39 21	894 0	50 8	(8)	1200 3
‡34 52	944 8			
3028 97	33005 2	104 9		
19 37	110 1		(9)	982 5
3014 01	33168 9		(10)	819 8

FUNDAMENTAL $1d—mf$

$1d = 28933\ 5$ $1d' = 28955\ 2$, $1d'' = 28968\ 8$

λ, Int	ν	Δν	m	mf
4585 92 (2)	21799 7		(3)	7133 9
85 87 (6)	799 5	21 5		
4581 41 (5)	21821 2	13 6		
4578 57 (4)	21834 8			
4098 55 (4)	24392 1	21 5	(4)	4541 5
94 94 (3)	413 6	13 7		
92 65 (2)	427 3			
3875 81 (4)	25793 9	21 8	(5)	3139 5
72 55 (3)	815 7	13 5		
70 51 (2)	829 2			
3753 37 (1)	26635 3	21 5	(6)	2298 1
50 35 (1)	656 8	14 1		
48 37 (1)	670 9			
3678 24 (2)	27179 4	21 6	(7)	1754 1
75 31 (2)	201 0	13 8		
73 45 (1)	214 8			
3628 60	27551 2	22 1	(8)	1382 3
25 69	573 3	12 0		
§ 24 11	585 3			
3594 08	27815 7	21 8	(9)	1117 7
91 26	837 5	13 8		
89 49	851 3			
3568 91	28009 6	24 3	(10)	923
66 12	033 9	13 9		
64 35	047 8			
3550 03	28158 5	23 5	(11)	774
47 38	182 0	14 3		
45 58	196 3			
3535 55	28273 8		(12)	660

* Terms calculated from combination $1d—2p$ are 12729 4, 12749 5, 12756 4

† Calculated, not observed

‡ Probably belongs to d series

§ See also d series

Ca TRIPLETS—*Continued*

DIFFUSE $1p$—md
$1p_1$=33988 7, $1p_2$=34094 6, $1p_3$=34146 9

λ, Int	ν	Δν	m	md'', d', d	λ, Int	ν	Δν	m	md'', d', d
19917 3	5019 6	13 3	(1)	28969 1	——	——	—	(7)	1848 9
864 3	32 9	22 2		955 2	3109 51	32150 3	9 6		38 7
771 1	55 1			933 5	3108 58	159 9			28 8
		105 6					105 4		
19506 8	5125 2	14 3			——	——			
452 6	39 5				3099 34	32255 7			
		52 1					—		
19310 3	5177 3				3095 29	32298 0			
4456 61(3)	22432 4	3 7	(2)	11556 4	——	——	—	(8)	1551 2
55 88(5)	436 1	5 6		552 6	3081 55	32441 9	7 7		47 0
54 77(9)	441 7			547 0	80 82	449 6			39 1
		105 9					105 4		
4435 67(8)	22538 3	3 7			3071 97	32543 2	4 1		
34 95(9)	542 0				71 58	547 3			
		52 1					52 6		
4425 43(9)	22590 4				3067 01	32595 8			
3644 99(0)	27427 3	1 7	(3)	6561 4	——	——	—	(9)	1272 7
44 76(3)	429 0	2 8		59 7	3055 55	32718 2	2 3		70 7
44 40(7)	431 8			56 9	55 32	720 5			68 2
		106 0					105 1		
3630 97(2)	27533 3	1 6			——	——	—		
30 75(6)	534 9				3045 75	32823 3			
		52 0					—		
3624 11(6)	27585 3				3041 05	32874 0			
3362 28(0)	29733 3	1 4	(4)	4255 5	——	——		(10)	1045 4
62 13(2)	734 7	1 8		54 0	——	——			
61 92(6)	736 5			52 2	3034 52	32944 8			
		105 8							
3350 36(2)	29839 1	1 5			——	——			
50 20(5)	840 6				3024 93	33049 2			
		52 2							
3344 51(5)	29891 3				3020 15	33101 5			
——	——	—	(5)	3002 4	3018 55	33119 1		(11)	869 6
3226 13(1)	30988 1	2 4		00 6					
25 88(5)	990 5			2998 2					
		105 8			3006 22	33254 9		(12)	733 8
3215 33(1)	31092 2	1 7							
15 15(3)	093 9				2996 67	33360 8		(13)	627 9
		52 3							
3209 93 (3)	31144 5				2988 98	33446 7		(14)	541 0
——	——	—	(6)	2268 2					
3151 28(1)	31724 1	5 3		64 5					
50 75(4)	729 4			59 3	2982 89	33515 2		(15)	473 5
		106 0							
3141 16(0)	31826 3	3 8							
40 78(2)	830 1								
		52 4							
3136 00(2)	31878 7								

Ca TRIPLETS—*Continued*

COMBINATIONS $1d—mp$

λ, Int.	ν	ν calc
6169 58(3)	16204 1	$1d—2p_1$ = 16204 1
6161 31(2)	225 9	$1d'—2p_1$ = 225 8
6156 08	239 7	$1d''—2p_1$ = 239 4
6169 03(2)	205 6	$1d'—2p_2$ = 205 7
6163 75(2)	219 5	$1d''—2p_2$ = 219 3
6166 44(2)	212 4	$1d''—2p_3$ = 212 4
4512 28(1)	22155 7	$1d—3p_1$ = 22155 7
07 85(0)	177 4	$1d'—3p_1$ = 177 4
05 00	191 4	$1d''—3p_1$ = 191 0
09 45(0)	169 6	$1d'—3p_2$ = 169 6
06 62	183 5	$1d''—3p_2$ = 183 2
07·42	179 5	$1d''—3p_3$ = 179 2
4065 44	24590 8	?$1d—4p_1$ = 24590 8
4062 49	608 7	?$1d'—4p_1$ = 24612 5

COMBINATION $2d—mf$

λ	ν	ν calc
22655 9	4412 9	$2d—3f$ = 4413 1
624 6	19 0	$2d'—3f$ = 4418 7
610 0	21 8	$2d''—3f$ = 4422 5
14278	7002	$2d—4f$ = 7005 5

COMBINATION $2p—md$

λ	
16200 0	Possibly part of incompletely observed group of six lines of combination $2p—3d$
162 2	
144 8	

Ca SINGLETS

PRINCIPAL $1S—mP$ *
$1S$ = 49304 8

λ, Int	ν	m	mP
4226 73(10*R*)	23652 4	(1)	25652 4
†2721 65	36731 8	(2)	12573 1
2308 58(2)	41678 8	(3)	7625 9
2275 49(1)	43933 3	(4)	5371 4
2200 78(1)	45425 0	(5)	3879 6
2150 78(1)	46480 5	(6)	2824 6
2118 68	47184 7	(7)	2120 3
2097 49	47661 3	(8)	1638 2
2082 73	47998 9	(9)	1305 9
2073 04	48223 2	(10)	1071 6
2064 77	48416 3	(11)	888 5

SHARP $1P—mS$
$1P$ = 25652 4

λ, Int	ν	m	mS
—4226 73(10*R*)	—23652 4	(1)	49304 8
10345 0	9664 2	(2)	15988 2
5512 98(4)	18134 0	(3)	7518 4
4847 29(2)	20624 4	(4)	5028 0
4496 16	22235 1	(5)	3417 3
4312 31	23183 0	(6)	2469 4
4203 22	23784 7	(7)	1867·7
4132 64	24190 9	(8)	1461 5
4084 5	24476	(9)	1176

Formerly known as SL1 (SL = 'single line") A strong series
† Abnormally faint
‡ Formerly known as SL3
§ Formerly known as SL2 Faint and diffuse in air, but of medium strength in vacuum arc

DIFFUSE $1P—mD$
$1P$ = 25652 4

λ, Int	ν	m	mD
	(—1802 9)	(1)	27455 3
7326 10(8)	13646 1	(2)	12006 3
5188 85(3)	19266 9	(3)	6385 5
4685 26(2)	21337 7	(4)	4314 7
4412 30	22657 7	(5)	2994 7

FUNDAMENTAL $1D—mF$ ‡
$1D$ = 27455 3

λ, Int	ν	m	mF
4878 13(5)	20494 0	(3)	6961 3
4355 10(5)	22955 3	(4)	4500 0
4108 55(1)	24332 7	(5)	3122 6
3972 58(1)	25165 6	(6)	2289 7
3889 14(1)	25705 5	(7)	1749 8
3833 96	26075 5	(8)	1379 8
3795 62	26339 0	(9)	1116 3
3767 42	26536 0	(10)	919 3

COMBINATION $1D—mP$ §

λ, Int	ν	ν calc
	(1803)	$1D—1P$ = 1802 9
6717 69(5)	14882 0	$1D—2P$ = 14882 2
5041 61(3)	19829 5	$1D—3P$ = 19829 4
4526 94(4)	22083 9	$1D—4P$ = 22083 9
4240 46(2)	23575 8	$1D—5P$ = 23575 7
4058 91(0)	24630 4	$1D—6P$ = 24630 7
3946 05(0)	25334 8	$1D—7P$ = 25333 0
3871 54	25822 3	$1D—8P$ = 25817 1

Ca SINGLETS—*Continued*

COMBINATION $1S—mD$ *

λ	ν	ν calc
4575 43	21849 9	$1S—1D$ = 21849 5
2680 36	37297 6	$1S—2D$ 37298 5
2329 33	42918 0	$1S—3D$ 42919 3
2221 91	44992 6	$1S—4D$ 44990 1

COMBINATION $1S—mS$

λ	ν	ν calc
2392 22	41789 8	$1S—2S$ = 41786 4
2257 40	44285 5	$1S—4S$ = 44276 8
2177 8	45883	$1S—5S$ = 45887 5

OTHER COMBINATIONS

λ, Int	ν	ν calc
7645 25(1)	13076 9	$1P—2P$ — 13079 3
4929 25	20281 4	$1P—4P$ = 20281 0
	3412	$2S—2P$ = 3415
	8359	$2S—3P$ = 8362
	19935 2	$1D—3S$ = 19936 9

Ca INTER-COMBINATIONS

λ	ν	ν calc
6572 78(3)	15210 3	$1S—1p_2$ = 15210 2
2734 82	36554 9	$1S—2p_2$ = 36554 6
3761 70	26576 2	$1p_2—3S$ = 26576 2

Possibly also $1D—2p_1$, $1D—2p_2$, $1D—3p_2$

Other Unclassified Lines of Ca

λ, Int	ν	Δν
6439 086(9)	15525 87	
5857 476(8)	17067 48	
5349 470(5)	18688 25	
5262 238(3)	18998 05	
4307 738(7)	23207 53	
4298 989(8)	23258 17	
3000 865(4)	33311 50	

Unclassified Triplets and Pairs of Ca

λ, Int	ν	Δν
4318 648(9)	23148 91	
4298 989(8)	254 76	105 85
89 363(9)	306 96	52 20
5601 283(5)	17848 11	
5594 464(8)	869 87	21 76
90 109(5)	883 79	13 92
5270 272(5)	18969 08	
64 237(3)	990 84	21 76
60 375(1)	19004 77	13 93
7202 161(2)	13880 89	
7148 123(3)	985 83	104 94
4302 525(9)	23235 66	
4283 008(9)	341 53	105 87
3006 864(5)	33247 58	
2997 309(4)	353 57	105 99
6499 648(4)	15381 20	
93 789(8)	395 08	13 88
6471 659(4)	15447 72	
62 576(9)	469 44	21 72
6455 606(3)	15486 15	
49 811(7)	500 05	13 90
5602 829(5)	17843 18	
5598 484(8)	857 03	13 85
5588 746(9)	17888 15	
81 973(6)	909 85	21 70
5265 559(5)	18986 07	
61 701(3)	999 99	13 92

* Faint and diffuse except in vacuum sources, last two wave-lengths difficult to determine

the line must belong to the series, because its "term" enters into combinations which appear in the spectrum (see also p 40) The terms quoted for the P series are averages from P itself and the combination $1D-mP$ Saunders remarks that the courses of the S and D series would have been difficult to trace but for the existence of parallel combination series In the D series it should be noted that the suggested first line has a negative frequency, it seems necessary to suppose its existence in order to give an appropriate connection with the F lines Support for the selected F series is given by the close approach of the terms to those of hydrogen (*i e*, μ is nearly unity), which is a general feature of such series

The limits chosen by Saunders have been adjusted to accord with the interrelations indicated by the various series and combinations, and are believed to have been found with considerable precision

In addition to combinations in each of the two groups of series, there are lines which result from combinations of terms taken from the singlet and triplet systems As Saunders remarks, this points to a close relation between the two systems

There are several interesting triplets and pairs which have not been found to belong to the regular system, although their separations are identical with those observed in the series These and the brighter unclassified single lines have been included in the tables, as further investigation of possible series or combinations is very desirable

The intensities shown in the table are those given by Crew and McCauley, as photographed in the vacuum arc The intensities of the additional lines observed by Saunders have not been stated, but it may be assumed that all the lines for which no intensities are quoted are of low intensity

Ionised Calcium (Ca+).

The enhanced lines of calcium form a system of pairs, of which but few occur outside the Schumann region The well-known H and K lines form the principal pair Crew and McCauley's wave-lengths have been adopted in the range which they cover, and the remainder are as given by Lyman, except $\delta(1)$, in which case the wave-lengths are the means of the values given by Meggers and Meissner The separation of the main pairs is 222 85, and that of the narrower fundamental pairs, as indicated by the satellite separation in δ (1) is 60 85

The limit 70325 29 was calculated by a Hicks formula from the less refrangible components of the first three σ pairs, giving the formula —

$$\sigma_1(m)=70325\ 29-4N/(m+1\ 205543-0\ 064899/m)^2$$

The $O-C$ ($\Delta\nu$) equal +0 01,* +0 04,* 0 00,* −18, −24 As shown by Hicks,† a more accurate representation of the series is obtained by putting $\mu>1$, and there is the additional advantage that $m=1$ then gives the first pair The first pair of δ occurs with negative sign, and this also is given by $m=1$, when μ in that series is taken to be greater than unity No combination lines have yet been recognised.

* Used in calculation of constants

† Proc Roy Soc , **91**, 452 (1915)

Ca^+ Doublets

Principal $1\sigma - m\pi$
$1\sigma = 95739\ 70$

λ, Int	ν	Δν	m	$m\pi_{1,2}$
3933 664(10*R*)	25414 41	222 85	(1)	70325 29
3968 465(10*R*)	191 56			548 14

Sharp $1\pi - m\sigma$
$1\pi_1 = 70325\ 29$ $1\pi_2 = 70548\ 14$

λ, Int	ν	Δν	m	$m\sigma$
—3933 664(10*R*)	—25414 41	222 85	(1)	95739 70
—3968 465(10*R*)	— 191 56			
3736 903 (9)	26752 55	222 91	(2)	43572 71
06 022 (9)	975 46			
2208 606 (3)	45263 26	222 71	(3)	25062 10
2197 791 (3)	485 97			
1851 3	54016	220	(4)	16310
43 8	236			
1698 9	58861	226	(5)	11463
92 4	59087			

Diffuse $1\pi - m\delta$
$1\pi_1 = 70325\ 29$, $1\pi_2 = 70548\ 14$

λ, Int	ν	Δν	m	$m\delta'$, δ
—8498 00 (8)	—11764 25	60 85	(1)	82089 52
—8542 15 (10)	— 703 44	222 89		028 73
—8662 11 (9)	— 541 36			
3181 283 (6)	31424 80	19 19	(2)	38900 47
79 340(10)	443 99	222 89		881 30
58 877(10)	647 69			
——	—	8 61	(3)	23017 56
2112 763 (2)	47316 34	222 89		008 95
03 239 (2)	530 58			
1815 0	55096		(4)	15232
07 8	316			
1680 5	59506		(5)	10815
74 1	733			

Fundamental $1\delta - m\varphi$
$1\delta = 82029$, $1\delta' = 82090$

λ	ν	Δν	m	$m\varphi$
1840 2	54341	65	(3)	27686
38 0	406			
1555 1	64304	66	(4)	17723
53 5	370			
1434 3	69720	58	(5)	12311
33 1	778			
1370 6	72960		(6)	9060
69 1	73040			

Strontium

Sr At wt = 87 63, At No = 38

The arc spectrum of strontium is generally similar to that of calcium, consisting of a system of triplets and a system of singlets The separations of the components of the triplets are greater than those of Ca in approximate proportion to the squares of the atomic weights, and corresponding triplets are displaced to the red with respect to those of Ca

The chief line of the singlet system is $\lambda 4607$, which is the only line of Sr developed in the bunsen flame, and is the leader of the *P* series As in the case of Ca, the intensities in *P* are somewhat irregular, and the series cannot be represented by a simple formula

Measurements of the arc and spark lines on the international system have been made by Hampe,* covering the region 7070 to 2428*A* Observations by Lorenser and

* Zeit Wiss Phot, 13, 348 (1914)

Sr TRIPLETS

PRINCIPAL $1s—mp$
$1s = 16897\ 8$

λ, Int	ν	Δν	m	$mp_{1,2,3}$
—7070 10(10)	—14140 2	394 2		31038 0
—6878 35(10)	— 534 4	186 8	(1)	432 2
—6791 05(5)	— 721 2			619 0
20263	4933 8		(2)	*11964 0
9597 0	10417 1		(3)	†6480 7

SHARP $1p—ms$
$1p_1 = 31038\ 0$, $1p_2 = 31432\ 2$, $1p_3 = 31619\ 0$

λ, Int	ν	Δν	m	ms
7070 10 (7)	14140 2	394 2		
6878 35 (7)	534 4	186 8	(1)	16897 8
6791 05 (6)	721 2			
4438 04 (4)	22526 2	394 2		
4361 71 (4)	920 4	186 8	(2)	8511 8
4326 44 (3)	23107 2			
3865 46 (4)	25862 8	394 5		
07 38 (4)	26257 3	187 0	(3)	5174 9
3780 46 (3)	444 3			
3628 37 (2)	27552 7	393 2		
3577 33 (1)	945 9	187 4	(4)	3485 7
53 5	28133 3			
3504 27 (2)	28528 5	394 1		
3456 52 (1)	922 6	187 3	(5)	2509 4
34 28 (1)	29109 9			

FUNDAMENTAL $1d—mf$
$1d = 27617\ 2$, $1d' = 27717\ 7$, $1d'' = 27777\ 6$

λ, Int	ν	Δν	m	mf'', f', f
4893 12	20431 2	1 8	(3)	7186 0
92 69 (2)	433 0	2 7		84 2
92 03 (6)	435 7			81 5
		100 5		
4869 19 (3)	20531 7	1 9		
68 74 (4)	533 6			
		59 7		
4855 08 (4)	20591 4			
			(4)	4571 3
4337 89	23046 2	1 0		70 9
37 70 (4)	047 2			70 0
4319 12	23146 4	0 5		
19·03 (3)	146 9			
		59 0		
4308 13 (2)	23205 4			

FUNDAMENTAL $1d—mf$ (*continued*).
$1d = 27617\ 2$, $1d' = 27717\ 7$, $1d'' = 27777\ 6$

λ	ν	Δν	m	mf'', f', f
4087 46	24458 2	99 6	(5)	3160 5
70 88	557 8	59 3		59 9
61 08	617 1			59 0
3950 65	25305 1	100 0	(6)	2314 5
35 10	405 1	58 0		12 6
26 14	463 1			12 1
3867 2	25851 2		(7)	1766 0

DIFFUSE $1p—md$
$1p_1 = 31038\ 0$, $1p_2 = 31432\ 2$, $1p_3 = 31619\ 0$

λ, Int	ν	Δν	m	md'', d', d
	(3260 4)	59 9	(1)	27777 6
30109 7	3320 3	100 5		717 7
29225 0	3420 8			617 2
		394 2		
27355 3	3654 6	59 9		
26914 5	3714 5			
		187 0		
26023 6	3841 6			
4971 65 (3)	20108 5	15 0	(2)	10929 5
67 93 (4)	123 5	23 1		914 5
62 24 (6R)	146 6			891 4
		394 2		
4876 06 (6)	20502 7	15 0		
72 49 (6)	517 7			
		186 6		
4832 08 (6)	20689 3			
4033 19 (0)	24787 3	4 9	(3)	6250 7
32 39 (3)	792 2	12 3		45 8
30 39 (4)	804 5			33 5
		394 2		
3970 05 (3)	25181 5	4 9		
69 27 (3)	186 4			
		186 9		
3940 8 1(4)	25368 4			

* The terms calculated from combinations $1d—2p$ are 11963 8, 12068 4, 12109 8 These values are further justified by combinations $1D—2p$

† The probable terms calculated from combinations $1d—3p$ are 6479 1, 6510 2, 6525 0

Sr TRIPLETS—*Continued*

DIFFUSE $1p-md$ (*continue*) $1p_1=31038\ 0$, $1p_2=31432\ 2$, $1p_3=31619\ 0$

λ, Int	ν	Δν	*m*	*md″*, *d′*, *d*
——	——		(4)	4072 0
3706 74	26970 2	6 1		67 5
05 90 (3)	976 3			61 7
3653 91 (2)	27360 2	4 8		
53 26 (3)	365 0			
		186 9		
3629 12 (3)	27547 1			
——	——		(5)	2869 8
3548 66	28171 7	4 5		66 3
48 09 (4)	28176 2			61 8
3500 11	28562 4	3 5		
3499 68 (4)	28565 9			
		186 8		
3477 37 (0)	28749 2			

λ	ν	Δν	*m*	*md″*, *d′*, *d*
——	——		(6)	2134 7
3458 47	28906 3	4·1		31 7
57 98	910 4			27 6
——	——			
3411 94	29300 5			
3390 67	29484 3			
3401 23	29392 8		(7)	1645 2 (*d*)

COMBINATIONS $1d-mp$

λ, Int	ν	ν calc
6386 51 (6)	15653 6	$1d\ -2p_1=15653\ 6$
45 76 (4)	754 2	$1d'\ -2p_1=\ 754\ 1$
21 77 (0)	814 0	$1d''-2p_1=\ 814\ 0$
88 25 (6)	649 3	$1d'\ -2p_2=\ 649\ 3$
63 93 (5)	709 1	$1d''-2p_2=\ 709\ 2$
80 74 (5)	667 8	$1d''-2p_3=\ 667\ 8$
4729 48 (1*n*)	21138 1	$1d\ -3p_1=21138\ 1$
07 1 (0*n*)	238 6	$1d'\ -3p_1=\ 238\ 6$
14 0 (0*n*)	207 5	$1d'\ -3p_2=\ 207\ 5$
04 0 (0*n*)	252 6	$1d''-3p_2=\ 252\ 6$

Sr SINGLETS

PRINCIPAL $1S-mP$ *
$1S=45936\ 5$ †

λ, Int	ν	*m*	*mP*
4607 34 (10*R*)	21698 4	(1)	24238 1
2931 88 (2)	34097 8	(2)	11838 7
2569 50 (2)	38906 4	(3)	7030 1
2428 11 (2)	41171 8	(4)	4764 7
2354 32 (1)	42462 1	(5)	3474 4
2307 4 (1)	43325 5	(6)	2611 0
2275 48 (1)	43933 3	(7)	2003 2
53 34 (1)	44304 8	(8)	1571 7
37 4 (1)	44680 8	(9)	1255 7
25 9 (1)	44911 5	(10)	1025 0

SHARP $1P-mS$
$1P=24238\ 1$

λ, Int	ν	*m*	*mS*
—4607 34 (10)	—21698 4	(1	45936 5
11242 3?	8892 5	(2)	15345 6
5970 10 (3)	16745 5	(3)	7492 6
5165 46(2)	19354 0	(4)	4884 1

DIFFUSE $1P-mD$
$1P=24238\ 1$

λ, Int	ν	*m*	*mD*
	(—1547 9)	(1)	(25786 8)
7621 54 (5)	13117 1	(2)	11121 0
5543 32 (5)	18034 7	(3)	6203 4

FUNDAMENTAL $1D-mF$ ‡
$1D=25786\ 8$

λ, Int	ν	*m*	*mF*
5156 07 (4)	19389 2	(3)	6397 6
4678 30 (4)	21369 3	(4)	4417 5
4406 11(1)	22689 4	(5)	3097 4
4252 97 (1)	23506 4	(6)	2280 4

* Formerly known as S L, (single line) No 1

† Limit derived from inter-combination $1S-1p_2=\nu 14504\ 3$

‡ Formerly known as S L, 3.

Sr SINGLETS—*Continued.*

COMBINATION $1D—mP$ *
$1D = 25786\ 8$

λ, Int	ν	*m*	ν calc
7167 24 (6)	13948 5	(2)	13948 1
5329 82 (5)	18757 2	(3)	18756 7
4755 47 (2)	21022 5	(4)	21022 1
4480 54 (2)	22312 5	(5)	22312 4
4313 18 (1)	23178 2	(6)	23175 8
4202 81 (1)	23787 0	(7)	23783 6

COMBINATION

λ	ν	ν calc
4961 48	20149 7	$1S—1D = 20149\ 7$†

Sr INTER-COMBINATIONS

λ	ν	ν calc
6892 62 (6)	14504 3	$1S—1p_2 = 14504\ 3$
7309 47 (6)	13677 1	$1D—2p_3 = 13677\ 0$
7287 44 (1)	718 5	$1D—2p_2 = 13718\ 4$
7232 24 (6)	823 2	$1D—2p_1 = 13823\ 2$

Unclassified Lines of Sr

λ, Int.	ν
20704 8	4828 5
9643 7	10366 3
7673 11 (6)	13029 0
7408 08 (3)	13495 1
7362 59 (1)	13578 5
7348 48 (1)	13604 5
7153 08 (4)	13976 1
6550 28 (5)	15262 3
6465 78 (1)	15461 8
6408 49 (9)	15600 0
5847 82 (1)	17095 7
5816 77 (2)	17186 9
5767 05 (2)	17335 1
5556 32 (1)	17992 5
5521 30 (1)	18106 7
5225 11 (5)	19133 0
4412 62 (3)	22655 9
4140 36 (2)	24145 7
4051 0 (1)	24678 3
3962 62 (2)	25228 7
3371 00 (1)	29656 3
3330 01 (4)	30021 3
3200 1	31240 0
3199 0 (2)	31250 8
3190 1 (2)	31338 0
3189 3 (2)	31345 8
2549 54 (1)	39210 9
2435 55	41046 0
2408 74	41502 9
2138 60?	46744 7
2047 28?	48829 6

Unclassified Triplets and Pairs of Sr

λ, Int	ν	Δν
4876 32 (6)	20501 6	393 9
4784 39 (4)	895 5	186 8
4741 99 (5)	21082 3	
4811 87(6*R*)	20776 2	394 1
4722 27 (6)	21170 3	
4531 35 (4)	22062 3	394 2
4451 80 (3)	456 5	
3366 34 (5)	29697 3	394 2
22 24 (5)	30091 5	186 9
01 74 (5)	30278 4	
3351 26 (6*R*)	29831 0	394 2
07 55 (4)	30225 2	
6446 70 (1)	15507 5	186 8
6369 96 (6)	694 3	
7438 29 (2)	13440 3	58 9
05 83 (2)	499 2	
6643 58 (4)	15048 0	59 8
17 28 (5)	107 8	
6546 82 (4)	15270 4	100 5
04 02 (6)	370 9	
6546 82 (4)	15270 4	59 8
21 29 (1)	330 2	
5693 00 (0)	17560 6	59 4
73 80 (0)	620 0	
5540 11 (5)	18045 2	59 7
21 83 (6)	104 9	
5534 80 (5)	18062 5	100 5
5504 17 (5)	163 0	59 8
5486 12 (5)	222 8	
5480 84 (7)	18240 3	100 2
50 91 (6)	340 5	
5256 90 (6)	19017 3	100 5
29 27 (5)	117 8	59 8
12 97 (2)	177 6	
5238 55 (6)	19084 0	59 7
22 20 (5)	143 7	
3182 3 (1)	31414 7	100 0
72 2 (1)	514 7	

* Formerly known as S I, 2
† Used for calculation of 1*D*

by Meggers have also been utilised in drawing up the tables. Other measures, with the vacuum arc as a source, have been communicated to the author by Prof. Saunders, who has also given valuable suggestions as to the allocation of many of the lines.

The p series is at present very imperfectly known, but it has been possible to calculate the probable terms with the aid of certain combinations. The presence of satellites in the f series is very clearly shown.

For the least refrangible components of the sharp series of triplets the formula from the first three lines is

$$s_1(m) = 31037{\cdot}98 - N/(m + 1{\cdot}631561 - 0{\cdot}083879/m)^2,$$

giving residuals $\Delta\nu = -1{\cdot}1$ and $-2{\cdot}9$ for $m = 4$ and 5. The three limits have therefore been adopted as 31038·0, 31432·2 and 31619·0 in accordance with the triplet separations.

The limits for p, d and f have been derived in the usual way.*

Limits for the singlet system have been based upon the combination $1S - 1p_2$, except in the case of F, for which the limit depends upon the probable combination $1S - 1D$.

As in calcium, there are numerous triplets and pairs which do not fall into the regular systems, and many lines for which places have not been found. These have been tabulated to facilitate further investigations.

Intensities have been inserted when available, and it may generally be assumed that the lines are faint when no intensity numbers appear, except for infra-red lines.

Ionised Strontium (Sr^+).

The enhanced lines of strontium form a pair system analogous with those of calcium and barium. As in the case of those elements, the arc is a sufficient stimulus to develop the lines, but they are relatively more important in the spark, where the ordinary arc lines tend to disappear. (*See* Pl. IV.)

Only one pair of the principal series has been identified. Using the limits calculated for the σ pairs, $\pi\infty$ ($=1\sigma$) is found to be $= 88{,}952$, and the Rydberg formula indicates a second π pair in the region of $\lambda 1810$ with $\Delta\nu$ about 300. No such pair has been noted, and it would seem that the simple Rydberg formula is not sufficiently exact to predict its position.

The sharp series is very closely represented by the formula

$$\sigma_1(m) = 64435{\cdot}80 - 4N/(m + 1{\cdot}304298 - 0{\cdot}083489/m)^2,$$

giving errors 0·0 for the first three lines, and $O - C(\Delta\nu) = +3{\cdot}5$ (or $\Delta\lambda = -0{\cdot}15A$) for

* Note.—Since the above was written, a further communication from Prof. Saunders indicates the observation of many additional lines in extension of several of the series, and new limits are given as follows:—

$1p_1 = 31026{\cdot}9$	$1s = 16887{\cdot}1$	$1P = 24227{\cdot}1$
$1p_2 = 31421{\cdot}1$	$1d'' = 27766{\cdot}0$	$1S = 45925{\cdot}6$
$1p_3 = 31607{\cdot}8$	$1d' = 27706{\cdot}3$	$1D = 25776{\cdot}3$
	$1d = 27606{\cdot}0$	

As the investigation is not completed, and the combinations and general arrangement of the series are not affected, it has not been thought necessary to adjust the tables to the new limits. Some of the new data, however, have been incorporated.

the fourth. With the same limit, and calculating from δ (2) and δ (3), we get the formula

$$\delta_1(m) = 64435\ 80 - 4N/(m + 1\ 560163 - 0\ 106710/m)^2$$

This represents δ_1 (4) very closely, but extrapolation to δ_1 (1) gives −8447 in place of −9959 The error, however, is considerably smaller than with the formulæ previously given by Lorenser and Fowler, in which case μ was put < 1 * Johanson has applied his formula† to this series, and with the limit 64323 3 adopted from the σ series he finds $a = 2\ 563879$, $b = -3\ 805663$, N being taken $= 4 \times 109675$ This gives residuals $(\Delta\lambda)$ 0 0,‡ 0 0,‡ 0 0,‡ −1 2, −1 4

Sr+ Doublets

Principal $1\sigma - m\pi$
$1\sigma = 88952\ 47$

λ, Int	ν	Δν	m	$m\pi_{1,2}$
4077 71 (10)	24516 67	801 46	(1)	64435 80
4215 52 (9)	23715 21			65237 26

Sharp $1\pi - m\sigma$
$1\pi_1 = 64435\ 80$, $1\pi_2 = 65237\ 26$

λ Int	ν	Δν	m	$m\sigma$
—4077 71 (10R)	—24516 67	801 46	(1)	88952 47
—4215 52 (9R)	—23715 21			
4305 46 (5)	23219 81	801 45	(2)	41215 99
4161 81 (3)	24021 26			
2471 63	40446 92	801 64	(3)	23988 79
23 59	41248 56			
2051 76	48722 98	801 98	(4)	15712 56
18 53	49524 96			

Fundamental $1\delta - m\varphi$
$1\delta = 74115\ 60$, $1\delta' = 74395\ 66$

λ, Int	ν	Δν	m	$m\varphi$
2165 92	46154 84	280 76	(3)	27960 4
52 84	46435 60			
*1778 8 (9)	56217	286	(4)	17896
69 8 (8)	56503			
*1620 7 (5)	61702	283	(5)	12412
13 3 (4)	61985			
*1538 ? (1)	65020		(6)	9096

Diffuse $1\pi - m\delta$
$1\pi_1 = 64435\ 80$, $1\pi_2 = 65237\ 26$

λ, Int	ν	Δν	m	$m\delta', \delta$
—10038 0	—9959 42	279 62	(1)	74395 66
—10328 0	—9679 80			115 60
		800 57		
—10915 4	—9158 85			
3474 90 (3)	28769 60	85 61	(2)	35666 20
64 47 (7)	28855 21			580 59
		801 44		
3380 72 (6)	29571 04			
2324 52	43006 40	39 46	(3)	21429 98
22 39	43045 86			389 94
		800 30		
2282 05	43806 70			
—	—		(4)	14330 8
1994 31	50126 3			309 5
1963 74	50906 5			
*1847 0	54142		(5)	10293
* 20 0	54945			

Unclassified Lines †

λ	ν
*1560 8?(1)	64070
*1532 3?(1)	65261

* λ vacuum † Not certainly Sr+

* Phil Trans, A **214**, 237 (1914)
† *See* p 36
‡ Used in calculation of constants.

Barium

Ba At. wt =137 4, At No =56

A careful study of all the available data for the arc lines of barium has recently been made by Saunders,* who has revised the previously recognised series, and has identified additional combinations The *f* series is remarkable for the presence of satellites, which are generally similar to those occurring in the *d* series Both the *f* and *d* series show curious irregularities in the satellite separations, the data show, however, that the normal triplet separations are maintained by the satellites throughout, and that it is the chief lines which are subject to irregular displacements There are also irregularities in the intensities of the lines in some of the series No simple formula of ordinary type will represent the series with reasonable accuracy

The data chiefly used by Saunders in addition to his own special observations were obtained by King, Randall, Meggers and Eder Observations of the arc and spark spectra, and comparisons with previous records, have also been given by Schmitz† for the region λ 7,060 to 2,214, and by George‡ for the region λ 7,060 to 8,210

The tables which follow are a re-arrangement of those given by Saunders, but in some cases the lines have been differently numbered Thus, in the *f* series, since μ usually approaches unity in these series, the first triplet has been called (3) in place of the (1) assigned by Saunders

The intensities in the barium spectrum have been very incompletely recorded, Kayser and Runge's estimates have been adopted so far as possible Many lines remain unclassified

Ionised Barium (Ba^+).

The enhanced lines of barium form a pair system, with satellites, similar to those of Mg, Ca, and Sr The leading members were recognised by Runge and Paschen,§ and additional members were subsequently traced by Saunders The series are here given according to Lorenser, except that the new wave-lengths determined by Schmitz have been utilised as far as possible Lines in the Schumann region are from observations by Lyman

Hicks‖ has adopted the same sets of lines, except for the first member of the *d* series, for which he has selected, as an inverted δ set,

λ (Rowland)	ν	$\Delta\nu$
—5853 91 (10*R*)	—17077 96	
—3148 6 (*ft*)	—16190 53	1690 59
—3497 07 (6*R*)	—15387 37	

The first line, however, is unduly strong, and the suggested satellite is not only misplaced, but has a separation out of the usual proportion The infra-red lines assigned by Lorenser are doubtless correct, as they show a satellite separation in agreement with $\Delta\nu$ of the related fundamental series

* Astrophys Jour, **51**, 23 (1920)
† Zeit Wiss Phot, **11**, 209 (1912)
‡ *Ibid*, **12**, 257 (1913)
§ Sitz d Berlin Akad, p 720 (1902)
‖ Proc Roy Soc, A **91**, 455 (1915)

Ba TRIPLETS

PRINCIPAL $1s—mp$
$1s = 15869\ 3$

λ, Int	ν	Δν	m	$mp_{1,2,3}$
—7905 80(7)	—12645 5			28514 8
		878 2		
—7392 44(7)	—13523 7		(1)	29392 8
		370 6		
—7195 26(6)	—13894 3			763 3
20712 0	4827 0			11042 3
		171 9		
21477 2	4655 1		(2)	214 2
		72 2		
	*4582 9			286 4
†10189 1	9812 1			6057 2
		80 1		
10272 9	9732 0		(3)	137 3
		49 6		
10326	9682 4			186 9

SHARP $1p—ms$
$1p_1 = 28514\ 8$, $1p_2 = 29392\ 8$, $1p_3 = 29763\ 3$

λ	ν	Δν	m	ms
7905 80(7)	12645 5			
		878 2		
7392 44(7)	13523 7		(1)	15869 3
		370 6		
7195 26(6)	13894 3			
4902 90(6r)	20390 5			
		878 2		
4700 45(6r)	21268 7			
		370 5	(2)	8124 3
4619 98(4r)	21639 2			
4239 56(2r)	23580 9			
		878 4		
4087 31(1n)	24459 3			
		370 4	(3)	4934 0
4026 30	24829 7			
3975 32(2r)	25148 3			
		878 3		
3841 15	26026 6			
		370 5	(4)	3366 5
3787 23	26397 1			
†3828 93	26110 3			
		878 2		
3704 23	26988 5		(5)	2404 5

COMBINATIONS

λ	ν	ν calc
4674 97	21390 5	$1d—2p_1 =$ 21390 7
4593 16	21771 5	$1d'—2p_1 =$ 21771 8
	[obscured]	$1d''—2p_1 =$ [21953 3]
4629 63	21600 0	$1d'—2p_2 =$ 21599 9
4591 07	21781 4	$1d''—2p_2 =$ 21781 4
4606 38	21709 0	$1d''—2p_3 =$ 21709 2
3790 27	26376 9	$1d—3p_1 =$ 26375 8
26227 44	3812 8	$2d—3f =$ 3813 0

* Calculated wave-number
† Provisionally placed
‡ Masked by a line of iron impurity

DIFFUSE $1p—md$
$1p_1 = 28514\ 8$, $1p_2 = 29392\ 8$, $1p_3 = 29763\ 3$

λ, Int	ν	Δν	m	md'', d', d
—22313 4	—4480 6			
		181 6		
—23255 3	—4299 0		(1)	32995 6
		380 8		
—25515 7	—3918 2			814 1
		878 0		433 0
—27751 1	—3602 6			
		181 5		
—29233 9	—3421 1			
		370 7		
—30933 8	—3231 9			
5818 91(4n)	17180 7			
		55 1		
5800 30(6R)	235 8		(2)	11333 9
		67 4		279 0
5777 70(10R)	303 2			211 6
		878 2		
5535 93	18058 9			
		55 0		
5519 12(8R)	113 9			
		370 7		
5425 55(8R)	18429 6			
			(3)	6320 1
4493 66(4v)	22247 6			
		23 0		267 3
4489 00(4v)	270 6			244 2
4332 96(4n)	23072 6			
		52 8		
4323 63(4v)	125 4			
		370 7		
4264 43(4n)	23443 3			
			(4)	4067 5
4087 31(1n)	24459 3			55 4
		14 5		
4084 87(1n)	473 8			41 0
3947 51	25325 4			
		12 2		
3945 61	337 6			
		370 6		
3890 57	25696 0			
			(5)	2888 7
3898 58	25643 3			71 4
		27 7		
3894 34	671 0			43 8
3771 93	26504 1			
		17 4		
3769 48	521 5			
		370 6		
3719 92	26874 7			
			(6)	2137 1
3789 72	26379 9			34 8
		10 7		
3788 18	390 6			24 2
3667 93	27255 7			
		2 4		
3667 60	258 1			
‡3618 72)				
			(7)	
3721 17	26865 7			1649 1
		2 3		
3720 85	868 0			1646 8
3603 40	27743 7			

Ba TRIPLETS—*Continued.*

FUNDAMENTAL $1d$—mf				$1d$=32433 0, $1d'$=32814 1, $1d''$=32995 6					
λ, Int	ν	Δν	m	mf'', f', f	λ, Int	ν	Δν	m	mf'', f', f
3997 92	25006 1		(3)	7426 8	——	——		(8)	1415 4
95 66(6)	020 2	14 1		7412 8	†3222 28	31025 1			07 8
93 40(10*R*)	034 4	14 2		7398 6	21 63	031 4	3 3		01 6
		381 1					381 3		
3937 88(6)	25387 3				3183 96	31398 6			
35 72(8*R*)	401 2	13 9			83 16	406 4	7 8		
		181 5					182 0		
3909 92(8*R*)	25568 8				3165 60	31580 6			
3596 33	27798 3		(4)	4634 6	——	——		(9)	1134 2
93 20(4*r*)	822 7	24 4		4610 4	3193 97	31300 2			32 8
79 67(4*R*)	927 7	105 0		4505 3	93 91	300 8	0 6		32 2
		381 1					383 2		
3547 70	28179 5				3155 67	31680 1			
44 66(6*R*)	203 6	24 1			‡ 55 34	683 4	3 3		
		181 6					181 3		
3524 97(6*R*)	28361 1				3137 70	31861 4			
*3421 48	29218 9		(5)	3213 8	——	——		(10)	932·9
21 01	222 9	4 0		10 1	†3173 72	31499 7			
20 32(4*R*)	228 8	5 9		04 2	† 73 69	500 0	0 3		
		381 2					381 8		
3377 39	29600 3				——	——			
76 98(4*R*)	603 9	3 6			3135 72	31881 5			
		181 6					181 9		
3356 80(6*R*)	29781 9				3117 94	32063 4			
——	——		(6)	2351 2	——	——		(11)	781·7
3323 06	30084 3			48 7	——	——			
22 80(4*r*)	086 7	2 4		46 3	3158 54	31651 1			
		381 0					380 5		
3281 77	30462 8				——	——			
81 50(4*r*)	465 3	2 5			3121 02	32031 6			
		181 8							
†3262 30(2*r*)	30644 6				——	——			
——	——		(7)	1790 5	——	——		(12)	664 7
†3262 24	30645 2			88 0	——	——			
61 96	647 8	2 6		85 2	3146 90	31768 3			
		380 8					380 6		
3222 44	31023 6				——	——			
† 22 19	026 0	2 4			3109 63	32148 9			
		181 4							
3203 70	31205 0				——	——			
					3137 80	31860 6		(13)	572 4
					3130 6	31934		(14)	499

* Much too strong, perhaps not a member of this series

† These lines somewhat doubtful, as they are not clearly resolved

‡ This may not belong to the series, triplet irregular

Ba SINGLETS

PRINCIPAL $1S-mP$
$1S=42029\ 4$

λ, Int	ν	m	mP
5535 53(10*R*)	18060 2	(1)	23969 2
3071 59(6*R*)	32547 2	(2)	9482 2
2702 65(4*R*)	36989 9	(3)	5039 5
2596 68(4*R*)	38499 5	(4)	3529 9
2543 2	39308	(5)	2721
*2500 2	39985	(6)	2044
*2473 1	40423	(7)	1606

SHARP $1P-mS$
$1P=23969\ 2$

λ, Int	ν	m	mS
—5535 53(10*R*)	—18060 2	(1)	42029 4
13201	7569 8	(2)	16399 4

FUNDAMENTAL $1D-mF$
$1D=30634\ 1$

λ, Int.	ν	m	mF
5826 29(8*R*)	17158 9	(2)	13475 2
4080 93	24497 4	(3)	6136 7
3789 74	26397 7	(4)	4254 4

COMBINATION $1D-mP$

λ, Int.	ν	m	ν calc
15000 4	6664 9	(1)	6664 9
4726 46(8*R*)	21151 7	(2)	21151 9
‡3905 98(2)	25594 7	(3)	25594 6
3688 35(2)	27104 5	(4)	27104 2

COMBINATION $1S-mF$

λ, Int.	ν	m	ν calc
3501 12(10*R*)	28554 3	(2)	28554 2
2785 26(8*n*)	35893 0	(3)	35892 7
2646 50	37774 8	(4)	37775 0

DIFFUSE $1P-mD$
$1P=23969\ 2$

λ	ν	m	mD
—15000 4	—6664 9	(1)	30634 1
?9831 7	10168 8	(2)	13800 4
?6233·59	16038 2	(3)	7931 0
?5267 03	18981 4	(4)	4987 8
?4877 69	20496 6	(5)	3472 6
?4663 60	21437 5	(6)	2531 7

COMBINATION $2S-mP$

λ, Int.	ν	m	ν calc
——	——	(2)	[6917 2]
8799 70(2*n*)	11360 9	(3)	11359 9
7766 80(2)	12871 8	(4)	12869 5

OTHER COMBINATIONS

λ, Int	ν	ν calc
†9527 0	10493 6	$1P-2F=10494\ 0$
3900 37(4*n*)	25631 5	$1S-2S=25630\ 0$

Ba INTER-COMBINATIONS

λ, Int	ν	ν calc
7911 36(6)	12637 1	§$1S-1p_2=12636\ 6$
3244 20	30816 6	§$1S-2p_2=30815\ 2$
11304 20	8844 1	$1d'-1P=\ 8844\ 9$
‡4284 90	23331 2	$1d'-2P=23331\ 9$
3599 40 (6)	27774 9	$1d'-3P=27774\ 6$
3413 84	29284 3	$1d'-4P=29284\ 2$

* Not positively identified as belonging to this series
† Very faint line
‡ Abnormally faint
§ This series is strong at low temperatures

The less refrangible components of the second, third, and fourth pairs of the sharp series lead to the formula

$$\sigma_1(m)=58712\ 5-4N/(m+1\ 438086-0\ 108104/m)^2$$

This gives the first line as —22099 4 in place of the observed —21952 4, and the fifth as 48057 in place of the observed 47999.

The limits assigned to the fundamental series follow the usual rules, but are considerably different from those independently calculated from the observed lines, namely, 71120 5 and 71696 4

Ba+ Doublets

Principal $1\sigma - m\pi$. $1\sigma = 80664\ 9$

λ, Int.	ν	Δν	*m*	$m\pi_{1,2}$
4554 04 (10*R*)	21952 4	1690 9	(1)	58712 5
4934 10 (9*R*)	20261 5			60403 4

Sharp $1\pi - m\sigma$. $1\pi_1 = 58712\ 5$, $1\pi_2 = 60403\ 4$.

λ, Int	ν	Δν	*m*	$m\sigma$
—4554 04 (10*R*)	—21952 4	1690 9	(1)	80664 9
—4934 06 (9*R*)	—20261 5			
4899 97 (8)	20402 6	1690 9	(2)	38309 9
4524 95 (7)	22093 5			
2771 35 (6)	36072 8	1690 6	(3)	22639 8
2647 28 (4)	37763 4			
2286 11	43728 9	1691	(4)	14983
2201 1	45420			
2082 7	47999		(5)	10714

Fundamental $1\delta - m\varphi$. $1\delta = 68097\ 6$, $1\delta' = 68674\ 3$

λ, Int	ν	Δν	*m*	$m\varphi$
2335 25 (8*R*)	42808 8	576 7	(3)	25288 8
2304 21 (8*R*)	43385 5			
1869 2	53499		(4)	14602
1849 5	54068			
1694 3	59021		(5)	9077
1677 9	59598			

Diffuse $1\pi - m\delta$. $1\pi_1 = 58712\ 5$, $1\pi_2 = 60403\ 4$

λ, Int	ν	Δν	*m*	$m\delta', \delta$
—10035 6	— 9961 8	576 7	(1)	68674 3
—10652 4	— 9385 1			097 6
		1689 1		
—12084 8	— 8272 7			
4166 02 (4)	23997 0	205 3	(2)	34715 5
4130 68 (8*R*)	24202 3			510 2
		1690 9		
3891 79 (6*R*)	25687 9			
2641 39 (4)	37847 5	94 7	(3)	20865 8
2634 80 (7)	37942 2			770 3
		1689 3		
2528 51 (5)	39536 8			
2235 4	44721	54	(4)	13991
2232 7	44775			938
		1691		
2154 0	46412			
2054 9	48649		(5)	10109
				064
1987 7	50294			

Unclassified Pair *

λ, Int	ν	Δν
5853 70 (8)	17078 5	1690 9
6496 90 (8)	15387 6	

* Zeeman effect is of δ type

Radium

Ra At wt = 226 4, At No = 88

Measurements of the spark spectrum of radium, between wave-lengths 6487 and 2709, were made by Runge and Precht,* of the arc and spark by Exner and Haschek,† and of the spark spectrum by Crookes ‡ The spark spectrum may, of course, include arc lines, just as the arc often includes spark lines

The series of arc lines have not yet been satisfactorily traced Analogy with the other elements of the alkaline earth group indicates that a triplet system and a

* Ann d Ph, **14**, 418 (1904)
† Wien Ber, **120**, IIa, 967 (1911)
‡ Proc Roy Soc, **72**, 295, 413 (1903).

system of singlets may be expected Hicks* has attempted to find the triplets, and has suggested an arrangement which gives separations 2050 and 832 ?, but the relative intensities and general fragmentary character of the suggested triplets leave the question very doubtful A further attempt has been made by the Misses Anslow and Howell,† who proceeded on the basis of $\Delta\nu$=about 3060 for the separation of the extreme components of the triplets as deduced from the spectra of calcium, strontium and barium Attention is drawn to a number of possible triplets with $\Delta\nu_1$, $\Delta\nu_2$=2016 64 and 1036 15, giving 3052 79 for the extreme members These intervals, however, are averages, and the individual differences seem to vary more than the probable errors of measurement The wave-numbers were not corrected to vacuum in this investigation, but when this correction is made the results are not sufficiently improved to establish confidence Furthermore, the intensities of the components of the triplets are irregular, and the suggested satellites call for further investigation

There is a strong line in the flame spectrum at λ 4825 94 I A

Ionised Radium (Ra^+)

Some of the lines of radium were identified by Runge and Precht as forming pairs analogous with corresponding pairs of Ca, Sr, and Ba ‡ These may now be certainly regarded as enhanced lines, although their behaviour in the arc has not been investigated The lines are not sufficiently numerous to permit the calculation of satisfactory formulæ, but by assuming the constant for these series to be $4N$, and using a simple Rydberg formula, the limit for the less refrangible components of the sharp series is found to be about 57863 Hicks, however, has found reason to believe that the true limit is nearer to 56653 23, and this has been adopted in the following table for the known lines of Ra^+ —

Ra^+ Doublets

Principal $1\sigma-m\pi$ 1σ=82862 05					Sharp $1\pi-m\sigma$ $1\pi_1$=56653 23, $1\pi_2$=61510 44				
λ, Int	ν	Δν	m	$m\pi_{1,2}$	λ, Int	ν	Δν	m	$m\sigma$
3814 43 (100) 4682 18 (50)	26208 82 21351 61	4857 21	(1)	56653 23 61510 44	—3814 43 (100) —4682 18 (50)	—26208 82 —21351 61	4857 21	(1)	82862 05
Diffuse $1\pi-m\delta$ $1\pi_1$=56653 23, $1\pi_2$=61510 44.					5813 63 (15) 4533 16 (10)	17196 20 22053 50	4857 30	(2)	39456 98
λ, Int	ν	Δν	m	$m\delta', \delta$					
4436 32 (20) 4340 67 (50) 3649 60 (50)	22534 90 23031 46 27392 49	496 56 4857 59	(2)	34118 1 33621 77					

Fues§ gives the limits as 1σ=80,000, $1\pi_1$=53785, $1\pi_2$=58645

* Phil Trans, A **212**, 64 (1913)
† Proc Nat Acad Sci, Wash, **3**, 409 (1917)
‡ Sitz d Berlin Akad, p 417 (1904)
§ Ann d Phys, **63** 17 (1920)

CHAPTER XV.

GROUP IIB —ZINC, CADMIUM, AND MERCURY

The elements zinc, cadmium, and mercury form a second branch of Group II of the periodic system, and their spectra have a general resemblance to those of the alkaline earth metals, which form the first branch Thus, the arc spectrum in each case comprises a triplet system and a singlet system, with combinations and inter-combinations The spectra of the ionised elements have not been completely investigated, but it is probable that they yield doublets as in the case of the alkaline earth metals

The elements, zinc, cadmium, and mercury, however, while showing the usual atomic weight relationship among themselves, are not united in this way with the alkaline earth metals

The sharp and diffuse series of triplets were identified by Rydberg, and by Kayser and Runge, and the work of Paschen* subsequently led to a knowledge of the principal series and of the single line systems, in addition to numerous combinations A further important contribution was made in Paschen's laboratory by K Wolff,† who traced the principal series of singlets in the Schumann region, and obtained wave-lengths which appear to be of remarkable accuracy

The spectra of zinc and cadmium in the Schumann region have also been observed by McLennan, Ainslie and Fuller ‡

The most complete lists of wave-lengths are those given by Kayser and Runge These have been supplemented in the ultra-violet for Zn and Cd by Huppers§ and by Eder ||

A partial revision of wave-lengths for Zn and Cd, based on photographs of vacuum arc spectra, has been made by Saunders,¶ and the new wave-lengths have been adopted in the tables which follow

ZINC

Zn At wt =65 38 , At No =30

The wave-lengths of the principal series of triplets, and of all the lines less refrangible than λ4810, have been adopted from the observations by Paschen For the sharp and diffuse series the revision and extension by Saunders have been utilised The remaining wave-lengths are mostly from the lists of Kayser and Runge and of Huppers, except in the region of short wave-lengths The adopted limits of the series are as determined by Saunders

Apart from lines which are probably due to impurities of lead and tin, there are very few tabulated lines which do not find places in one or other of the series The combination line $1S-2D$, at 1601 09, has not previously been recognised as such

The " single line " spectrum of zinc, as observed by McLennan,** is represented by the prominent line λ 3075 88, being the inter-combination $1S-1p_2$

* Ann d Phys , **29**, 625 (1909) , **30**, 747 (1909) , **35**, 860 (1911) , **40**, 602 (1913)
† Ann d Phys , **42**, 825 (1913)
‡ Proc Roy Soc , A **95**, 316 (1919)
§ Zeit Wiss Phot , **13**, 46 (1914)
|| *Ibid* , **13**, 20 (1914) , **14** 137 (1915).
¶ Privately communicated
** Proc Roy Soc , A **91**, 485 (1915)

Zn TRIPLETS

PRINCIPAL $1s—mp$. $1s = 22094\ 4$

λ, Int.	ν	Δν	m	$mp_{1,2,3}$
–4810 53(10*R*)	–20781 9	388 9	(1)	42876 3
–4722 16(10*R*)	–21170 8	189 8		43265 2
–4680 20(10*R*)	— 360 6			455 0
13054 89	7657 9	56 2	(2)	14436 5
151 50	01 7	26 7		492 7
197 79	7575 0			519 4
6928 33(8)	14429 5	21 1	(3)	7664 9
38 48(6)	408 4	19 8		86 0
43 22(4)	398 6			95 8
5772 00(10)	17320 2	10 3	(4)	4774 2
75 43(8)	309 9	4 7		84 5
77 02(6)	305 2			89 2
5308 51(8)	18832 4	5 6	(5)	3262 0
10 11(6)	826 8	2 6		67 6
10 84(4)	824 2			70 2
5068 53(4)	19724 1	3 7	(6)	2370 3
69 49(2)	720 4	1 9		74 0
69 98(0)	718 5			75 9

SHARP $1p—ms$
$1p_1 = 42876\ 3$, $1p_2 = 43265\ 2$, $1p_3 = 43455\ 0$

λ, Int	ν	Δν	m	ms
4810 53(10*R*)	20781 9	388 9	(1)	22094 4
4722 16(10*R*)	21170 8	189 8		
4680 20(10*R*)	360 6			
3072 07(10*R*)	32541 9	388 7	(2)	10334 4
35 81(10*R*)	930 6	190 1		
18 38(8*r*)	33120 7			
2712 48(8*R*)	36855 8	390 1	(3)	6020 5
2684 06(8*R*)	37245 9	189 9		
70 44(6*r*)	435 8			
2567 80(6*r*)	38932 2	390 2	(4)	3944 1
42 32(6*r*)	39322 4	190 0		
30 09(2*r*)	512 4			
2493 32(4*n*)	40095 1	390 2	(5)	2781 2
69 38(2*r*)	485 3	190 2		
57 80(1*r*)	674 5			
2449 72(1)	40808 3	388 5	(6)	2068 0
26 63(1)	41196 8	190 1		
15 48(1)	386 9			
2421 82	41278 7	388 6	(7)	1597 6
2399 23	667 3	190 7		
88 30	858 0			
2402 82	41605 5		(8)	1270 8

* Observations discordant, and enhanced line involved.

DIFFUSE $1p—md$
$1p_1 = 42876\ 3$, $1p_2 = 43265\ 2$, $1p_3 = 43455\ 0$

λ, Int	ν	Δν	m	md'', d', d
3345 96(4)	29878 2	4 0	(2)	12997 6
45 51(8*R*)	882 2	5 4		994 2
44 91(10*R*)	887 6			988 7
		389 4		
3302 91(8*R*)	30267 6	3 2		
02 56(8*R*)	270 8			
		190 3		
3282 28(8*R*)	30457 9			
——	——		(3)	7187 0
2801 07(7)	35690 2	2 2		85 9
00 90(8)	692 4			83 9
2770 95(6*R*)	36078 0	1 5		
70 84(8*R*)	079 5			
		190 2		
2756 43(6*R*)	36268 2			
				md
2608 55(8*R*)	38323 0	389 4	(4)	4553 3
2582 38(8*R*)	712 4	189 5		
69 80(6*R*)	901 9			
2515 81(6)	39737 6	387 1	(5)	3138 7
2491 48(6)	40124 7	189 9		
79 74(4)	314 6			
2463 47(4)	40580 8	388 5	(6)	2295 5
40 11(4)	969 3			
* ——	—			
2430 79(1)	41126 4	387 0	(7)	1749 9
08 13(1)	513 4	190 1		
2397 15	703 5			
2409 06	41497 4	386 9	(8)	1378 9
2386 80	884 3	190 1		
76 01	42074 4			
2393 85	41761 0	388 5	(9)	1115 3
71 78	42149 5	193 2		
60 96	342 7			
2382 22	41964 8		(10)	911 5
60 96	42342 7			
2374 36	42103 7		(11)	707 6
2367 72	42221 9		(12)	654 4

FUNDAMENTAL $2d—mf$
$2d = 12988\ 7$, $2d' = 12994\ 2$, $2d'' = 12997\ 6$

λ	ν	Δν	m	mf
16498 6	6059 5	3 1		
490 3	6062 6	2 4	(3)	6931 3
· 483 7	6065 0			
			(4)	[4442 3]

Zn TRIPLETS—*Continued*

COMBINATION $1p$—mf
$1p_1 = 42876\ 3$, $1p_2 = 43265\ 2$, $1p_3 = 43455\ 0$

λ, Int	ν	ν calc
2781 23 (4*v*)	35944 1	$1p_1 - 3f = 35945\ 0$
51 39 (2*v*)	36334 6	$1p_2 - 3f = 36333\ 9$
36 86 (2*n*)	527 4	$1p_3 - 3f = 36523\ 7$
2600 94 (2*n*)	38436 1	$1p_1 - 4f = 38434\ 0$
2575 06 (2*n*)	822 4	$1p_2 - 4f = 822\ 9$
62 61 (2*n*)	39011 0	$1p_3 - 4f = 39012\ 7$

COMBINATIONS

λ	ν	ν calc
24045 7	4157 6	$2p_3 - 2s = 4158\ 3$
13792 4	7248 4	$2p_1 - 3d' = 7250\ 6$
13784 8	7252 4	$2p_1 - 3d = 7252\ 6$
10979 4	9105 5	$1s - 2d = 9105\ 7$
3515 11(1*n*)	28440 5	$1p_1 - 2p_1 = 28439\ 8$

Zn SINGLETS

PRINCIPAL $1S$—mP
$1S = 75766\ 8$

λ, Int	ν	*m*	*mP*
* 2138 61 (8*R*)	46745 1	(1)	29021 7
† 1589 76 (10)	62902	(2)	12857 9‡
† 1457 56 (8)	68608	(3)	7160 6‡
† 1404 19 (4)	71215	(4)	4559 1‡
† 1376 87 (2)	72629	(5)	3141 7‡

SHARP $1P$—mS
$1P = 29021\ 7$

λ, Int.	ν	*m*	*mS*
—2138 61 (8*R*)	—46745 1	(1)	75766 8
11055 4	9043 0	(2)	19978 7
5182 0 (5)	19292 2	(3)	9729 5
4298 38 (2)	23258 0	(4)	5763 7
§ 3965 7	25209 2	(5)	3812 5
§ 3799 4	26312 3	(6)	2709 4

DIFFUSE $1P$—mD
$1P = 29021\ 7$

λ Int	ν	*m*	*mD*
6362 37 (10)	15713 1	(2)	13308 6
4629 88 (8*r*)	21592 8	(3)	7428 9
§ 4113 6	24302 5	(4)	4719 2
§ 3883 ±2	25746∓13	(5)	3276 ±13

COMBINATION $2S$—mP
$2S = 19978\ 7$

λ	ν	*m*	*mP*
—11055 4	—9043 0	(1)	29021 7
14039 5	7120 8	(2)	12857 9
7799 33 (6)	12818 1	(3)	7160 6
6479 24 (5)	15429 6	(4)	4559 1
5937 67 (3)	16837 0	(5)	3141 7
5654 39 (1)	17680 5	(6)	2298 2
5485 98 (1)	18223 2	(7)	1755 5

COMBINATION

λ, Int	ν	ν calc
† 1601 09 (4)	62457 5	$1S - 2D = 62458\ 2$

Zn INTER-COMBINATIONS

λ, Int	ν	ν calc
15682 1	6375 0	$2D - 3f = 6377\ 3$
6239 22 (6)	16023 2	$1P - 2d'' = 16024\ 1$
6238 00 (8)	16026 4	$1P - 2d' = 16027\ 5$
‖3075 88 (8*R*)	32501 6	$1S - 1p_2 = 32501\ 6$
4292 86 (2)	23288 0	$1p_2 - 2S = 23286\ 5$
†1632 11 (4)	61270 4	$1S - 2p_2 = 61274\ 1$

Unclassified Lines of Zn

λ, Int	ν
10970 7	9113 2
7478 75 (6)	13367 5
6470 98 (4)	15449 3
6102 17 (2)	16383 1
6022 (1)	16601
?4101 79 (2)	24372 8
3739 97 (4)	26730 6
2623 78 (1)	38101 6
?2393 81	41761 7
?2063 8	48438

Wolff		McLennan, Ainslie and Fuller	
λ vac	ν	λ vac	ν
1649 87 (5)	60610 8		
		1510 4 (1)	66207
		1491 5 (1)	67047
1486 20 (5)	67285 7	1486 2 (6)	67286
		1478 5 (2)	67636
1476 01 (2)	67750 2	1477 6 (4)	67677
1474 67 (3)	67811 8		
1450 82 (1)	68926 5	1451 1 (4)	69915
		1445 0 (3)	69204

* Eder's λ in spark is 2138 55
† Wolff λ vac
‡ Determined from combination $2S$—mP
§ New values by Saunders
‖ Used for calculation of $1S$

Ionised Zinc (Zn^+)

Certain pairs of lines in the spectrum of zinc, with a mean separation of 876, were noted by Rydberg, and further attention was directed to them by Paschen, who also observed their behaviour in the magnetic field

The lines in question are definitely enhanced lines, and there can be no doubt that they originate in the ionised element The magnetic resolutions suggest that one of the pairs is of the principal, and the other of the sharp series type A third pair, in the orange, noted by Paschen as having the same separation, gives a magnetic resolution of the diffuse series type On the basis of N for the series constant, Paschen assigned one pair to $0\,5\sigma - 1\pi_{1,2}$ and the other to $1\pi_{1,2} - 1\,5\sigma$, in the notation of Ritz When $4N$ is adopted for the series constant, and in the notation of this Report, these become respectively $1\sigma - 1\pi_{1,2}$ and $1\pi_{1,2} - 2\sigma$ The lines are too few to permit a trustworthy calculation of limits, but approximate values, as shown below, have been derived by the use of Rydberg's table, with $4N$ for constant *

Zn^+ Doublets

Principal $1\sigma - m\pi$ $1\sigma = 147{,}544$					Sharp $1\pi - m\sigma$ $1\pi_1 = 98190$, $1\pi_2 = 99062$				
λ	ν	Δν	m	$m\pi_{1,2}$	λ	ν	Δν	m	$m\sigma$
*2025 49	49354 7	872 2	(1)	98190	—2025 49	—49354 7	872 2	(1)	147,544
61 96	48482 5			99062	— 61 96	—48482 5			
Unclassified Pair, Diffuse Type					†2558 01	39081 1	874 6	(2)	59,109
λ	ν	Δν			02 03	955 7			
6214 65	16086 6	873 9			* λ Eder				
5894 43	960 5				† λ Huppers				

There are numerous other enhanced lines of zinc, especially in the ultra-violet, and further investigation of the series is needed Attention should be specially drawn to the pair of lines 4923 98(10) and 4911 63(10), with wave-numbers 20303 1 and 20354 2 There is an analogous pair in cadmium, and since they do not occur in the true arc spectrum, † it is possible that they correspond with 4481 of magnesium, and may be members of a series of the fundamental type

Cadmium

Cd At wt = 112 4, At No = 48

The authorities for wave-lengths are generally the same as for zinc, and the adopted limits are as communicated by Saunders

The "single line" or "resonance" spectrum, as observed by McLennan, is represented by the combination line $1S - 1p_2$, λ3261 04

* Fues gives $1\pi_1 = 109650$, $1\pi_2 = 110{,}520$, $1\sigma = 159{,}000$ (Ann d P, **63**, 18, 1920)
† Fowler and Payn, Proc Roy Soc, **72**, 255, Plate 14 (1903)

Cd TRIPLETS

PRINCIPAL $1s—mp$
$1s = 21054\ 7$

λ, Int	ν	Δν	m	$mp_{1,2,3}$
—5085 88 (10*R*)	—19656 8	1171 1	(1)	40711 5
—4799 91 (10*R*)	—20827 9	541 9		41882 6
—4678 19 (10*R*)	—21369 8			42424 5
13979 22	7151 6	174 1	(2)	13903 1
14327 99	6977 5	70 7		14077 2
14474 62	6906 8			14147 9
7346 2 (10)	13608 7	71 5	(3)	7446 0
85 0 (9)	537 2	25 4		7517 5
98 9 (5)	511 8			7542 9
6099 18 (8)	16391 1	33 1	(4)	4663 6
6111 52 (6)	358 0	12 5		4696 7
6116 19 (4)	345 5			4709 2
5598 77 (6)	17856 1	18 8	(5)	3198 6
5604 68 (4)	837 3	6 9		3217 4
5605 85 (2)	830 4			3224 3
5339 50 (1)	18723 2		(6)	2331 5

SHARP $1p—ms$
$1p_1 = 40711\ 5$, $1p_2 = 41882\ 6$, $1p_3 = 42424\ 5$

λ, Int	ν	Δν	m	ms
5085 88 (10*R*)	19656 8	1171 1	(1)	21054 7
4799 91 (10*R*)	20827 9	541 9		
4678 19 (10*R*)	21369 8			
3252 52 (8*r*)	30736 5	1170 6	(2)	9975 6
3133 19 (8*r*)	31907 1	541 2		
3080 93 (6*r*)	32448 3			
2868 26 (6*r*)	34854 1	1171 3	(3)	5857 3
2775 00 (6*r*)	36025 4	541 8		
2733 88 (4*r*)	567 2			
2712 40 (6*r*)	36857 1	1168 0	(4)	3856 6
2629 06 (4*r*)	38025 1	541 5		
2592 14 (2*r*)	566 6			
2632 23 (2*r*)	37979 1	1170 6	(5)	2732 9
2553 53	39149 7	541 3		
2518 70	691 0			
2585 07	38672 1	1173 8	(6)	2037 6
2508 91	39845 9	541 8		
2475 25	40387 7			
2554 51	39134 7	1171 1	(7)	1576 8
2480 28	40305 8			
——	——			
2533 91	39452 9	1173 3	(8)	1257 0
2460 72	40626 2			
——	——			

DIFFUSE $1p—md$
$1p_1 = 40711\ 5$, $1p_2 = 41882\ 6$, $1p_3 = 42424\ 5$.

λ, Int	ν	Δν	m	$md'', d'd$
3614 43 (4)	27659 0	11 8	(2)	13052 4
12 89 (8*R*)	670 8	18 2		13040 7
10 51 (10*R*)	689 0			13022 5
		1171 1		
3467 61 (8*R*)	28830 1	11 9		
66 18 (10*R*)	842 0			
		542 2		
3403 60 (10*R*)	29372 3			
2981 89 (1)	33526 0	6 2	(3)	7185 3
81 34 (4*R*)	532 2	8 0		7179 5
80 63 (8*R*)	540 2			7171 3
		1171 3		
2881 23 (4*P*)	34697 3	5 5		
80 77 (8*R*)	702 8			
		542 1		
2836 90 (8*R*)	35239 4			
——	——		(4)	4549 9
2764 19 (2*R*)	36166 2			4546 3
63·89 (6*R*)	170 2			4541 3
——	——			
2677 64 (8*d*)	37335 2			
2639 50 (6*R*)	37874 6			
2660 40 (4*r*)	37577 2		(5)	3139 2
2580 27 (2*n*)	38744 1			3138 5
44 72 (2*n*)	39285 3			3134 5
2602 18 (2*n*)	38417 8		(6)	2294 5
2525 30 (1*n*)	39587 3			
2491 16	40129 9			
2565 88	38961 3		(7)	1751 3
2491 16	40129 9			
57 87	40673 4			
2541 64	39332 9		(8)	1379 3
2468 25	40502 2			
35 58	41045 5			
2524 68	39597 1		(9)	1114 3
2452 22	40767 1			
19 90	41311 4			
2512 37	39791 0		(10)	920 3
2440 51	40962 6			
2502 99	39940 3		(11)	771 6
2431 73	41110 5			
2495 88	40054 0		(12)	658 1
25 04	41223 9			
2490 23	40144 8		(13)	566·7

Cd TRIPLETS—*Continued*

FUNDAMENTAL $2d—mf$
$2d = 13022\ 5$, $2d' = 13040\ 7$, $2d'' = 13052\ 4$

λ	ν	*m*	*mf*
16482 2	6065 5		
16433 8	6083 4	(3)	6957 1
16401 5	6095 4		
11630 8	8595 6	(4)	4445 1 *

COMBINATION $1p—mf$

λ, Int	ν	ν calc
2961 48 (4*v*)	33757 1	$1p_1—3f = 33754\ 4$
2862 30 (2*v*)	34926 7	$1p_2—3f = 34925\ 5$
2818 73 (1*v*)	35466 5	$1p_3—3f = 35467\ 4$
2756 78 (3*n*)	36263 5	$1p_1—4f = 36266\ 4$
2670 66 (3*n*)	37432 9	$1p_2—4f = 37437\ 5$
2632 26 (2*n*)	37978 9	$1p_3—4f = 37979\ 4$

OTHER COMBINATIONS

λ, Int	ν	ν calc
14852 9	6730 4	$2p_1—3d = 6731\ 8$
14474 6	6906 8	$2p_2—3d = 6905\ 9$
14329 6	6976 8	$2p_3—3d = 6976\ 6$
14354 5	6964 6	$2p_3—3d'' = 6962\ 6$
3729 06 (4*r*)	26808 8	$1p_1—2p_1 = 26808\ 4$
3005 41 (1*r*)	33263 7	$1p_1—3p_1 = 33265\ 5$
3595 49 (1*n*)	27804 7	$1p_2—2p_2 = 27805\ 4$
2903 13 (1*n*)	34435 9	$1p_2—3p_1 = 34436\ 6$
2908 74 (1*r*)	34369 1	$1p_2—3p_2 = 34365\ 1$

* The term 4*f* is somewhat uncertain

Cd SINGLETS

PRINCIPAL $1S—mP$
$1S = 72538\ 8$

λ, Int	ν	*m*	*mP*
2288 02 (10*R*)	43692 2	(1)	28846 6
*1669 29 (10)	59905 7	(2)	12633 2
*1526 85 (8)	65494 3	(3)	7044 6
*1469 39 (6)	68055 5	(4)	4483 4
*1440 18 (3)	69435 8	(5)	3103 1
*1423 23 (1)	70262 7	(6)	2276 2

SHARP $1P—mS$
$1P = 28846\ 6$

λ, Int.	ν	*m*	*mS*
—2288 02(10*R*)	—43692 2	(1)	72538 8
10394 7	9617 3	(2)	19229 3
5154 68 (6*r*)	19394 5	(3)	9452 1
4306 82 (4*n*)	23212 5	(4)	5634 1
3981 77 (2*r*)	25107 4	(5)	3739 2
†3818 5	26180 9	(6)	2665 7
†3723 2	26851 0	(7)	1995 6

COMBINATIONS

λ	ν	ν calc
* 1688 58 (2,	59221 4	$1S—1D = 59219\ 5$
39086 9	2557 7	$3P—4P = 2557\ 8$

DIFFUSE $1P—mD$
$1P = 28846\ 6$

λ, Int	ν	*m*	*mD*
‡6438 47 (10)	15527 4	(2)	13319 2
4662 51 (8*r*)	21441 7	(3)	7404 9
†4140 5	24144 9	(4)	4701 7
†3905 1	25600 3	(5)	3246 3

COMBINATION $2S—mP$
$2S = 19229\ 3$

λ	ν	*m*	*mP*
§—10394 7	— 9617 3	(1)	28846 6
15154 8	6596 8	(2)	12632 5
8200 2	12191 5	(3)	7037 8
6778 10	14749 3	(4)	4480 0
6198 22	16129 2	(5)	3100 1
5895 8	16956 5	(6)	2272 8
5715 8	17490 5	(7)	1738 8
?5598 06	17858 4	(8)	1380 9?

* λ vac, Wolff
† Saunders
‡ The fundamental line of the international system of wave-lengths
§ λ Paschen (Trans Int Sol Union 4,81, 1913)

Cd SINGLETS—*Continued*

Cd INTER-COMBINATIONS		
λ, Int	ν	ν calc
15713 5	6362 2	$2D-3f=$ 6362 1
11268 4	8872 0	$2D-4f=$ 8874 1
6329 97(8)	15793 5	$1P-2d''=15794$ 2
6325 19(10)	15805 4	$1P-2d'=15805$ 9
4615 39	21660 6	$1P-3d''=21661$ 3
4614 17	21666 3	$1P-3d'=21667$ 4
4114 5	24297 4	$1P-4d''=24296$ 7
		$1P-4d'=24300$ 3
5297 64(2)	18871 1	$1P-2s=18871$ 0
*1942 29(6)	51485 6	$1S-1s=51484$ 1
†3261 04(10)	30656 2	$1S-1p_3=30656$ 2
*1710 51(3)	58462 1	$1S-2p_2=58461$ 6
*1537 83(1)	65026 7	$1S-3p_2=65021$ 3
4413 06(6)	22653 7	$1p_2-2S=22653$ 3
3082 68	32429 6	$1p_2-3S=32430$ 5
7132 1	14017 3	$1s-3P=14016$ 9
6031 39	16575 3	$1s-4P=16574$ 7
5568	17954 8	$1s-5P=17954$ 6
5324	18777 7	$1s-6P=18781$ 9
3649 59(2r)	27392 5	$1p_1-2D=27392$ 3
3499 94(4r)	28563 7	$1p_2-2D=28563$ 4

* λ vac , Wolff

† Used in calculation of $1S$

‡ Dr Catalan has suggested that this may be the combination $2p_2-3p_2$ giving ν=6559 7

§ The wave-number is 352 6 lower than that of the line $1S-1p_2$

‖ The wave-number is 351 9 lower than that of the line $1S-1P$

¶ Other lines in the Schumann region have been recorded by McLennan, Ainslie and Fuller (Proc Roy Soc , A **95**, 330, 1919)

Unclassified Lines of Cd ¶

λ, Int	ν
‡15257 3	6552 4
6128 66 (2)	16312 3
5783 93 (4)	17284 5
5637 22 (5)	17734 3
4615 75 (2)	21658 9
4511 34 (5)	22160 2

λ	ν	Δν
§3298 97 (4)	30303 6	
2748 61 (2)	36371 3	
2657 00 (2)	37625 2	
2654 55 (1)	37660 0	
2329 27 (10)	42918 6	1169 6
2267 48 (5)	44088 2	543 5
2239 86 (5)	44631 7	

λ	ν
‖ 2306 61 (5)	43340 3
2262 29 (1)	44189 3
2230 40 (1)	44820 9
2170 04 (1)	46067 7

λ vac	ν
*1993 07 (1)	50173 8
*1682 12 (1)	59448 8
*1647 78 (2)	60687 7
*1571 40 (1)	63637 5

IONISED CADMIUM (Cd^+).

The spectrum of ionised cadmium is similar to that of zinc, and Paschen has suggested that one pair belongs to the principal and another to the sharp series. Limits have been calculated by the Rydberg formula on the supposition that the series constant is $4N$, but they can only be regarded as roughly approximate * The wave-lengths of the principal and sharp pairs are by Huppers , those of the unclassified pair by Eder

* Fues gives $1\pi_1=103{,}880$, $1\pi_2=105{,}350$, $1\sigma=150{,}500$.

Cd+ DOUBLETS

PRINCIPAL $1\sigma - m\pi$ $1\sigma = 140225\ 7$					SHARP $1\pi - m\sigma$ $1\pi_1 = 93607\ 2$, $1\pi_2 = 96090\ 0$				
λ, Int	ν	Δν	m	$m\pi_{1,2}$	λ, Int	ν	Δν	m	$m\sigma$
2144 39 (8*R*) 2265 04 (8*R*)	46618 5 44135 7	2482 8	(1)	93607 2 96090 0	—2144 39 (8*R*) —2265 04 (8*R*)	—46618 5 —44135 7	2482 8	(1)	140225 7
Unclassified Pair of Cd+					2748 61 (10) 2573 0 (10)	36371 3 38853 4	2482 1	2)	57236 2
λ	ν	Δν							
2321 13 (8) 2194 60 (4)	43069 3 45552 1	2482 8							

As in the case of zinc, enhanced lines are numerous, more especially in the ultra-violet. The pair of lines 5378 24 (10), 5337 54 (10), wave-numbers 18588 3 and 18730 0, corresponds with the 4924 pair of zinc The separations of the two pairs are approximately proportional to the squares of the atomic weights

Observations of the spark spectrum of cadmium in the Schumann region have lately been published by McLennan *

MERCURY

Hg At wt =200 4, At No =80

The wave-lengths for mercury are taken from Cardaun,† Eder and Valenta,‡ Kayser and Runge,‡ Paschen,§ Stiles,‖ Wiedmann¶ and Wolff ** The series arrangement is mainly due to Paschen In addition to the lines given, there are nearly 300 which have not yet been classified Under certain conditions, mercury yields also a "rich line spectrum," which was first observed by Eder and Valenta ††

A large number of the mercury lines, even the sharp ones, are resolvable, under high dispersion, into several components ‡‡ In general, only the mean wave-lengths are included in the tables

The limits $1s$ of the principal series of triplets and $2S$ of the singlet series $2S - mP$ have been taken from Wiedmann, and corrected to the International Scale The other limits have then been calculated from observed lines

The Hicks formula is found to be inadequate to express the series of mercury except for the higher members Generally speaking, for values of m lower than 5, the formulæ are not even approximately applicable

* Proc Roy Soc, A **98** 106 (1920)
† Zeit f Wiss Phot, **14**, 89 (1915)
‡ Kayser Handbuch der Spektroscopie, **6**
§ Ann d Phys, **29**, 662 (1909), **30**, 750 (1909), **35**, 869 (1911), Jahrb d Rad. u Elek, **8**, 178
‖ Astrophys Jour, **30**, 48 (1909)
¶ Ann d Phys, **38**, 1041 (1912)
** Ann d Phys, **42**, 835 (1913)
†† Denk Wien Akad, **61**, 401 (1894)
‡‡ Cardaun, loc cit Wendt, Dissert Tubingen, 1911 Janicki, Ann d Phys, **39**, (1912) Nagaoka and Takamine, Proc Phys Soc Vol XV (1912), &c, &c

Wiedmann has adopted a more complex grouping for the diffuse triplet series than that given here Each member of the series, according to his arrangement, consists of one of the tabulated diffuse triplets (excluding the third chief line) together with the corresponding member of the combination series $1p-mD$ He then calls attention to a remarkable relation between this series on the one hand, and an association of the diffuse singlet series with the combination series $1P-md''$, d', on the other The wave-number differences between corresponding members are found to be constant throughout the series, as shown in the following table for the first two members With the present classification of the series, however, this relation is a necessary consequence, the constant differences being represented by $1p_{1,\ 2,\ 3}-1P$ *

m	Diffuse Singlets and $1P-md''$, d'		Wave Number Differences	Diffuse Triplets, as given by Wiedmann	
	λ	ν		ν	λ
			10025 7	27290 2	3663 28
	5790 66	17264 5	14656 5	31921 0	3131 84
			16424 0	33088 5	2967 52
			10025 8	27293 2	3662 88
2	5789 69	17267 4	14656 5	31923 9	3131 56
			16423 8	33091 2	2967 28
			10025 8	27353 3	3654 83
	5769 60	17327 5	14656 5	31984 0	3125 66
			—	—	—
			10025 9	33021 2	3027 48
	4347 50	22995 3	14656 7	37652 0	2655 13
			—	—	—
			10025 9	33041 6	3025 62
3	4343 64	23015 7	14656 8	37672 5	2653 68
			16424 1	39439 8	2534 77
			10026 0	33065 1	3023 47
	4339 23	23039 1	14656 7	37695 8	2652 04
			—	—	—

All the measures given in the tables are on the International Scale except those of Wolff in the extreme ultra-violet The infra-red measures of Paschen have been adjusted in accordance with his correction of their original values †

* Since the above was written it has been shown by H Dingle (Proc Roy Soc , A **100**, 167) that it is possible to regard the spectrum as exhibiting a system of quadruplet series, the separations in the subordinate series being respectively 10025 2, 4630 6, 1767 3 The suggested quadruplet system includes all the terms of the tabulated triplet and singlet systems, with the exception of those of the sharp series of singlets

† Ann. d Phys , **36**, 197 (1911).

Hg TRIPLETS

PRINCIPAL $1s—mp$
$1s = 21830\ 8$

λ, Int	ν	Δν	m	$mp_{1,2,3}$
—5460 74(10)	—18307 5			40138 3
		4630 6	(1)	
—4358 34(10)	—22938 1			44768 9
		1767 3		
—4046 56(10)	—24705 4			46536 2
11287 15(10)	8857 3			12973 5
		1545 6	(2)*	
13673 09(6)	7311 7			14519 1
		145 5		
13950 76(2)	7166 2			14664 6
6907 53(10)	14473 0			7357 8
		356 6	(3)	
7082 01(4)	14116 4			7714 4
		20 2		
7092 20(1*r*)	14096 2			7734 6
5803 55(4*r*)	17226 1			4604 7
		164 0	(4)	
†5859 32(4*r*)	17062 1			4768 7
		37 1		
5872 12(2)	17025 0			4805 8
5354 05(4*r*)	18672 4			3158 4
		106 3	(5)	
‡5384 70(3*r*)	18566 1			3264 7
		14 9		
5389 01(1)	18551 2			3279 6
5120 65(3*r*)	19523 4			2307 4
		66 2	(6)	
5138 09(1)	19457 2			2373 6
		7 6		
5140 10(1)	19449 6			2381 2
4980 82(3*r*)	20071 5			1759 3
		43 0	(7)	
4991 5(2)	20028 5			1802 3
4890 27(2*r*)	20443 2			1387 6
		27 7	(8)	
4896 9 (1)	20415 5			1415 3
4827 1 (2)	20710 7			1120 1
		21 9	(9)	
4832 2 (1)	20688 8			1142 0

p_1	ν	Δν	m	mp_1
4782 1 (1)	20905 6		(10)	925 2
4748 1 (1)	21055 2		(11)	775 6
4722 8 (1)	21168 0		(12)	662 8
4701 8 (1)	21262 5		(13)	568 3
4685 3 (1)	21337 3		(14)	493 5
4672 7 (1)	21394 8		(15)	436 0
4662 4 (1)	21442 3		(16)	388 5
4653 4 (1)	21483 8		(17)	347 0

DIFFUSE $1p—md$
$1p_1 = 40138\ 3$, $1p_2 = 44768\ 9$, $1p_3 = 46536\ 2$

λ, Int	ν	Δν	m	md'', d', d
3662 88 (4*r*)	27293 2			12845 1
		60 1	(2)	
3654 83 (6)	27353 3			12785 0
		35 1		
3650 15(10)	27388 4			12749 9
		4630 7		
3131 56 (7)	31923 9			
		60 1		
3125 66 (8)	31984 0			
		1767 3		
2967 28 (5)	33691 2			
3025 62 (2)	33041 6			7095 5
		23 5	(3)	
3023 47 (4)	33065 1			7073 2
		21 5		
3021 50 (5)	33086 6			7051 7
		4630 9		
2653 68 (4)	37672 5			
		23 3		
2 52 04 (5)	37695 8			
		1767 3		
2534 77 (4)	39439 8			
2805 42 (1)	35635 0			4502 7
		12 1	(4)	
2804 46 (2)	35647 1			4491 0
		12 5		
2803 48 (4)	35659 6			4478 7
		4631 6		
2482 72 (3)	40266 6			
		11 5		
2482 01 (4)	40278 1			
		1767 2		
2378 34 (3)	42033 8			
			(5)	3110 2
2699 50 (1*n*)	37033 1			3104 5
		8 9		
2698 85 (3*n*)	37042 0			3096 3
		4632 1		
2399 74 (2)	41658 9			
		6 3		
2399 38 (3)	41665 2			
		1767 0		
2202 09 (2*n*)	43425 9			
2639 93 (3*n*)	37868 8			2279 4
			(6)	
2352 48 (1*n*)	42495 8			2273 1
2258 87 (1)	44256 8			2269 5
2603 15 (2*n*)	38403 8		(7)	
2323 30 (1*n*)	43029 5			1739 4
				1734 5

* Paschen hesitates between this triplet and (12390 7), 13950 76, (?), the latter being indicated by a formula The line $1S—2p_3$, however, afterwards discovered by Wolff, indicates that the above triplet is the true one

† Has satellites λ5860 10 and λ5868 08

‡ Has satellite λ5385 79

Hg TRIPLETS—*Continued*

SHARP $1p—ms$
$1p_1=40138\ 3$, $1p_2=44768\ 9$, $1p_3=46536\ 2$

λ, Int	ν	Δν	*m*	*ms*
5460 74(10)	18307 5	4630 6		
4858 34(10)	22938 1	1767 3	(1)	21830 8
4046 56(10)	24705 4			
3341 48 (6)	29918 3	4630 8		
2893 60 (5)	34549 1	1767 3	(2)	10219 9
2752 78 (4)	36316 4			
2925 41 (4)	34173 4	4630 8		
2576 29 (3)	38804 2	1767 4	(3)	5964 7
2464 06 (2)	40571 6			
2759 70 (3)	36225 3	4630 8		
2446 90 (2)	40856 1	1767 4	(4)	3912 8
2345 43 (1)	42623 5			
2674 99 (2)	37372 5	4632 1		
2379 99 (1)	42004 6	—	(5)	2765 0
2625 24 (2)	38080 7	4630 8		
2340 60 (1)	42711 5	—	(6)	2057 5
2593 41 (1)	38548 0		(7)	1590 3

* Stated by Paschen to be a double line with separation=10 A U

FUNDAMENTAL $2d—mf$
$2d=12749\ 9$, $2d'=12785\ 0$, $2d''=12845\ 1$

λ, Int.	ν	*m*	*mf*
17193 (1)	5814 8		
17108 5 (1)	5843 5	(3)	6939 9
16938 9 (2)	5902 0		
12020 2 (1)	8317 2		
—	—	(4)	4433 6
*11886 6 (1)	8410 6		

COMBINATION $1p—mf$

λ, Int	ν	ν calc
3011 05 (1*n*)	33201 4	$1p_1—3f=33198\ 4$
2462 60 (1)	37830 5	$1p_2—3f=37829\ 0$
2524 71 (1*r*)	39596 9	$1p_3—3f=39596\ 3$
2799 83 (2)	35706 1	$1p_1—4f=35704\ 7$
2478 1 (1)	40342 1	$1p_2—4f=40335\ 3$
2374 02 (2*n*)	42110 2	$1p_3—4f=42102\ 6$

OTHER COMBINATIONS

λ, Int	ν	ν calc
3680 01 (5)	27166 1	$1p_1—2p_1=27164\ 8$
3050 46 (1*n*)	32772 5	$1p_1—3p_1=32780\ 5$
3085 29 (1*n*)	32402 5	$1p_1—3p_2=32403\ 7$
3144 48 (2*r*)	31792 6	$1p_2—2p_1=31795\ 4$
3305 09 (1*r*)	30247 7	$1p_2—2p_2=30249\ 8$
2672 67 (1*n*)	37404 9	$1p_2—3p_1=37411\ 1$
3135 76 (2*n*)	31881 0	$1p_3—2p_3=31871\ 6$
36258 (2)	2757 3	$2p_1—2s = 2753\ 6$
23263 (3)	4297 6	$2p_2—2s = 4299\ 2$
22489 (3)	4445 4	$2p_3—2s = 4444\ 7$

Hg SINGLETS

PRINCIPAL $1S—mP$
$1S=84178\ 5$

λ	ν	*m*	*mP*
*1849 57	54065 7	(1)	30112 8
*†1402 72	71290 6	(2)	12887 9

DIFFUSE $1P—mD$
$1P=30112\ 8$

λ Int	ν	*m*	*mD*
5790 66 (10*r*)	17264 5	(2)	12848 3
4347 50 (6*n*)	22995 3	(3)	7117 5
3906 40 (4*n*)	25591 8	(4)	4521 0
3704 22 (1)	26988 6	(5)	3124 2
3592 97 (1)	27824 4	(6)	2288 4
3524 27 (2)	28366 7	(7)	1746 1
3478 98 (1)	28736 4	(8)	1376 4
3447 22 (1)	29001 0	(9)	1111 8

SHARP $1P—mS$
$1P=30112\ 8$

λ, Int	ν	*m*	*mS*
—1849 57	—54065 7	(1)	84178 5
10139 67 (24)	9859 7	(2)	20253 1
4916 04 (4*r*)	20335 9	(3)	9776 9
4108 08 (2*n*)	24335 4	(4)	5777 4
3801 67 (2)	26296 8	(5)	3816 0

* λ vac, Wolff

† Paschen obtains this line by assuming λ13570 68 as the value of $2S—2P$. He questions the truth of this, however, and the value of $2P$ which it gives leads to a line for $1s—2P$ which has not been observed, and which is unexpectedly close to $1s—2p_1$. It is probable, therefore, that λ1402 72 and λ13570 68 do not take part in the above series, but are combination lines, associated by the fact that their wave-number difference is equal to $1S—2S$

Hg SINGLETS—*Continued*

FUNDAMENTAL $2D—mF$
$2D = 12848\ 3$

λ, Int.	ν	m	mF
16918 3 (2)	5909 2	(3)	6939 1
*11886 6 (1)	8410 6	(4)	4437 7

COMBINATION $1P—mF$
$1P = 30112\ 8$

λ	ν	ν calc
4313 3 (1 *v*)	23177 7	$1P—3F = 23173\ 7$
3893 89 (1*n*)	25674 2	$1P—4F = 25675\ 1$

* Stated by Paschen to be a double line with separation = 10 A U
† Used in calculation of Principal series

COMBINATION $2S—mP$
$2S = 20253\ 1$

λ, Int	ν	m	mP†
—10139 67 (24)	—9859 7	(1)	30112 8
13570 68 (?)(4)	7366 9 (?)	(2)	12886 2 (?)
6716 45 (?)(5)	14884 8 (?)	(3)	5368 3 (?)
6234 35 (8)	16035 8	(4)	4217 3
‡5803 55 (4*r*)	17226 1	(5)	3027 0
5549 28 (3*r*)	18015 4	(6)	2237 7
5393 50 (2)	18535 8	(7)	1717 3
5290 1 (2)	18897 9	(8)	1355 2
5218 9 (2)	19155 7	(9)	1097 4
5165 8 (1)	19352 2	(10)	900 9
5128 9 (1)	19492 0	(11)	761 1

‡ This line occurs also as $1s—4p_1$ It is very diffuse, and is considered by Paschen to arise from both sources

Hg INTER-COMBINATIONS

COMBINATION $1p—mD$
$1p_1 = 40138\ 3$, $1p_2 = 44768\ 9$, $1p_3 = 46536\ 2$

λ, Int	ν	ν calc
3663 28 (5)	27290 2	$1p_1—2D = 27290\ 0$
3131 84 (7)	31921 0	$1p_2—2D = 31920\ 6$
2967 52 (1)	33688 5	$1p_3—2D = 33687\ 9$
3027 48 (2)	33021 2	$1p_1—3D = 33020\ 8$
2655 13 (4)	37652 0	$1p_2—3D = 37651\ 4$
——*	——	$1p_3—3D = 39418\ 7$
2806 84 (1)	35616 9	$1p_1—4D = 35617\ 3$
2483 83 (2)	40248 6	$1p_2—4D = 40247\ 9$
2379 46	42013 8	$1p_3—4D = 42015\ 2$
2700 92 (1)	37013 7	$1p_1—5D = 37014\ 1$
2400 52 (0)	41645 4	$1p_2—5D = 41644\ 7$
——	——	$1p_3—5D = 43412\ 0$

COMBINATION $1p_2—mS$

λ	ν	ν calc
—2536 52 (10*n*)	—39412 6	$1p_2—1S = -39409\ 6$
4077 83 (7*r*)	24515 9	$1p_2—2S = 24515\ 8$
2856 94 (1)	34992 4	$1p_2—3S = 34992\ 0$
2563 90 (1)	38991 7	$1p_2—4S = 38991\ 5$

* Probably hidden by strong diffuse line λ2536 52 (ν = 39412 6)

COMBINATION $1P—md$
$1P = 30112\ 8$

λ Int	ν	ν calc
5789 69 (2)	17267 4	$1P—2d'' = 17267\ 7$
5769 60 (10*r*)	17327 5	$1P—2d' = 17327\ 8$
——	——	
4343 64 (2)	23015 7	$1P—3d'' = 23016\ 3$
4339 23 (4)	23039 1	$1P—3d' = 23039\ 6$
——	——	
3903 64 (2)	25609 9	$1P—4d'' = 25610\ 1$
3901 90 (2*n*)	25621 3	$1P—4d' = 25621\ 8$
——	——	
3702 36 (1)	27002 3	$1P—5d'' = 27002\ 6$
3701 44 (1)	27008 8	$1P—5d' = 27008\ 3$
——	——	
3591 48 (1)	27835 9	$1P—6d'' = 27833\ 4$
3590 95 (1)	27840 0	$1P—6d' = 27839\ 7$
——	——	
——	——	
3523 00 (1)	28377 2	$1P—7d' = 28373\ 4$
——	——	
——	——	
3477 85 (1)	28745 5	$1P—8d' =$
——	——	

Hg INTER-COMBINATIONS—*Continued.*

COMBINATION $1S—mp_2$		
λ, Int	ν	ν calc
2536 52 (10*n*)	39412 6	$1S—1p_2=39409\ 6$
*1435 63	69655 8	$1S—2p_2=69659\ 4$

COMBINATION $1P—ms$		
λ	ν	ν calc
12070 23 (1)	8282 7	$1P—1s=\ 8282\ 0$
5025 56 (3)	19892 8	$1P—2s=19892\ 9$
4140 03 (1)	24147 9	$1P—3s=24148\ 1$
3815 84 (1)	26199 3	$1P—4s=26200\ 0$

* λ vac , Wolff

COMBINATION LINE		
λ, Int	ν	ν calc.
17071 54 (2)	5856 2	$2p_1—3D=5856\ 0$

COMBINATION $1s—mP$		
λ	ν	ν calc
—12070 23 (1)	—8282 7	$1s—1P=-\ 8282\ 0$
?	?	
6072 63 (5)	16462 9	$1s—3P=\ 16462\ 5$
5675 86 (5)	17614 5	$1s—4P=\ 17613\ 5$
5316 69 (3*v*)	18803 6	$1s—5P=\ 18803\ 8$
5102 42 (2*v*)	19593 1	$1s—6P=\ 19593\ 1$
4970 13 (1*v*)	20114 7	$1s—7P=\ 20113\ 5$
4883 1 (1)	20474 6	$1s—8P=\ 20475\ 6$
4822 3 (1)	20731 3	$1s—9P=\ 20733\ 4$

IONISED MERCURY (Hg^+)

The enhanced lines of mercury do not appear to have been investigated in relation to possible series Rydberg, however, noted a pair of lines in the ultra-violet which appeared to be analogous with the pairs of ionised zinc and cadmium which have already been mentioned The wave-lengths of these lines as given by Cardaun are shown below, together with the wave-numbers and separation

λ, Int	ν	Δν
2847 83 (8*n*)	35104 16	9829 3
2224 82 (3*n*)	44933 44	

These lines have been found to give Zeeman resolutions of the type of D_2 and D_1 of sodium, and possibly represent a principal pair They are among the enhanced lines identified as such by Steinhausen

For the pairs of Zn, Cd, Hg, the values of Δν divided by the squares of the atomic weights are respectively 204, 197, 246.

CHAPTER XVI

GROUP IIIA —SCANDIUM, YTTRIUM, AND RARE EARTHS

Series in the elements of this sub-group have not yet been clearly identified From analogy with previous groups it would be expected that the *arc* spectra would resemble the elements of Group IIIB , and give series of doublets The *spark* spectra, on the other hand, might show triplets The difficulty of analysing the spectra is increased by the fact that the (enhanced) lines of the ionised elements are well developed even by the stimulus of the electric arc, and that the two spectra have only been partially separated in most cases

Hicks has stated* that he has found evidence of doublet series of *S* and *D* types in Sc, Y, La and Yb, but details have only been given for Sc A tentative arrangement of the possible two series of this element† suggested the limits $1\pi_1=37950$ for the sharp series, and $1\sigma=22282$ for the principal series, with the doublet separation $\Delta\nu=320\ 8$

The question of constant differences in some of these spectra has been investigated by Paulson, but the details are too extensive for quotation

Probably the most important contribution to the analysis of the spectra is that of Popow,‡ who based his results on observations of the effects of a magnetic field which were made in Paschen's laboratory at Tubingen

Popow did not succeed in identifying any complete series, but only some combination groups, which will be best understood by reference to the corresponding combinations of calcium or strontium The combinations in question are those indicated by $1d-2p$ Being connected with a triplet system, each term has three values, but of the nine possible combinations only six appear In the form adopted by Popow, the strontium group, with our notation and numeration, would be represented thus —

				15668	$2p_3$
				41	
		15649	60	15709	$2p_2$
		105		105	
15654	100	15754	60	15814	$2p_1$
$1d$		$1d'$		$1d''$	

The *p* and *d* terms may here be regarded as co-ordinates, and 15649, for instance, is to be read as $1d'-2p_2$ The differences $1d'-1d$, $1d''-1d'$ give the separations of the fundamental series , $2p_1-2p_2$, $2p_2-2p_3$ give the separations in the second member of the principal series

Scandium (Sc At wt =44 1 , At No =21) —A combination group of this type, according to Popow, is composed of the lines —

λ (Rowd)	ν
2563 30 (2)	39000 8
60 35 (3)	045 6
55 90 (2)	113 7
52 46 (3)	166 2
45 24 (2)	276 99
40 94 (1)	344 05

* Phil Trans , A **212** 34 (1913)
† Hicks, Phil Trans , A **213**, 409 (1914).
‡ Ann d Phys , **45**, 163 (1914)

The suggested arrangement is as follows —

				39000 80	p_3
				112 88	
		39045 57	68 11	39113 68	p_2
		231 42		230 37	
39166 23	110 76	39276 99	67 06	39344 05	p_1
d		d'		d''	

In terms of the Ritz equation, Popow designates the group as $3d'-3p'$, which becomes $1(?2)d-2p$ in the notation of the present report

It is of importance to note that, according to the tables of Exner and Haschek, the lines in question are probably of the enhanced type

Yttrium (Y At wt =88 8, At No =39) —Two groups are given by Popow for Yttrium, designated respectively $3d'-2p'$ and $3d'-3p'$ The wave-numbers are

				22604 07	$1p_3$
				331 20	
		22730 31	204 96	22935 27	$1p_2$
		871 22		870 90	
23196 67	404 86	23601 53	204 64	23806 17	$1p_1$
$2d$		$2d'$		$2d''$	
				31207 57	$2p_3$
				75 27	
		31077 98	204 86	31282 84	$2p_2$
		159 47		159 46	
30832 61	404 84	31237 45	204 85	31442 30	$2p_1$
$2d$		$2d'$		$2d''$	

It may be deduced that the separations of the narrow triplets of the fundamental series are probably 405 and 205, while those of the first member of the principal series, and therefore the main separations in the subordinate series, would be 870 and 331

Lines of the first group are included among the enhanced lines given by Lockyer, those of the second group were not within the range of his investigation, and the observations of Exner and Haschek merely indicate that with one exception the lines are strong in both arc and spark

Lanthanum (La At wt =139 0, At No =57) —The following group for lanthanum is given by Popow as the combination $3d'-3p'$ —

				29889 59	$2p_3$
				375 19	
		29568 35	696 43	30264 78	$2p_2$
		1043 44		1043 63	
29953 03	658 76	30611 79	696 62	31308 41	$2p_1$
$2d$		$2d'$		$2d''$	

The separation Δd (=658 76) is here smaller than δd (=696 6), whereas in the other elements considered it is greater An irregularity in the arrangement of the

satellites in the related diffuse triplets is therefore suggested, if the combinations have been correctly identified

The available evidence does not very strongly point to the above lines being of the enhanced type, but Exner and Haschek's observations suggest that two of the lines are enhanced In the visible spectrum the only enhanced lines tabulated as such by Lockyer are λ4192 5 and 4099 7

From the data for Sc and Y, Popow deduces the formulæ—

$$0\ 529 \log \Delta p = \log A - 0\ 395$$
$$0\ 652 \log \delta p = \log A - 0\ 305$$

where A=At wt , $\Delta p = p_2 - p_1$, $\delta p = p_3 - p_2$

He then calculates that for Al, Δp=92, δp=53 5, which do not compare favourably with the separations of the probable triplet, 128, 64 It may be observed, however, that in the atomic weight relation Al belongs to the Ga, In, Tl sub-group, and agreement need not be expected with the elements of the first sub-group At all events, in the first and second groups the sub-groups do not show a common atomic weight relation

The general result of the discussion of the three elements is to suggest that the enhanced lines probably form triplet series

Of the " rare earths " having atomic numbers ranging from 57 to 71, many have been examined by Paulson* for " constant differences " Numerous lines of this class have been found, but it is scarcely possible to give any useful summary of the results Europium, however, is possibly of special interest, as in some arrangements of the periodic table it is suggested that this element should fall in Group II , between Cd and Hg Paulson finds four pairs of strong lines with separation 1669 7, and twelve weaker pairs with the same separation Hicks,† on the other hand, considers that the spectrum consists of triplets, having separations 2631 and 1004, the limit of the sharp series ($s_1 \infty$) being 40364 The diffuse series suggested by Hicks, however, is very imperfect, and the question cannot be considered settled one way or the other

As bearing on the place of gadolinium in the periodic table, Hicks thinks it probable that this element falls in Group IIIB , between indium and thallium, on the ground that there is a large number of doublets of separation about 5000 No details are given, and this separation does not appear among those noted by Paulson

There are no data relating to the spectrum of actinium

* Astrophys Jour , 40, 298 (1914) *See also* p 26
† Phil Trans , A 212, 59 (1913)

CHAPTER XVII.

GROUP IIIB —THE ALUMINIUM SUB-GROUP

The arc spectra of the elements Al, Ga, In, and Tl, forming a sub-group of Group III of the periodic table, present series of doublets The subordinate series were early identified by Rydberg and by Kayser and Runge, and the principal series were afterwards found by Paschen The series have a general resemblance to those of the alkali metals, but the separations are greater as compared with the increase of atomic weights Also, in these spectra the first principal pair occurs with negative sign, and the other members of the principal series lie on the red side of the subordinate series, whereas in the alkali metals the principal series lie on the more refrangible side of the sharp and diffuse series As in the case of the alkali metals, there are very few lines which have not been placed in one or other of the four main series, or are to be accounted for as combinations

The spectrum of boron probably lies mainly in the region of short wave-lengths, and complete series have not yet been traced

Little progress has been made in the detection of regularity in the spark spectra of these elements

BORON

B At wt =11 0, At No =5

The arc spectrum of boron in the region ordinarily observed is of remarkable simplicity, consisting of a close pair of lines in the ultra-violet, for which wave-lengths have been given by several observers The values from Rowland's measures are —

λ	ν	$\Delta\nu$
2497 73 (10*R*)	40024 3	15 3
96 78 (8*R*)	039 6	

Rydberg was probably right in supposing this to be the first pair of the sharp and principal series, but the formulæ which he suggested for the series depended upon the use of spark lines, and are probably therefore of no significance

Dr M A Catalán * has recently drawn attention to a second pair of arc lines, observed by Sr Piña de Rubies, which have a separation practically identical with that of the original pair, namely—

λ	ν	$\Delta\nu$
2089 49	47843 2	14 9
88 84	58 1	

An extension of the observations into the region of shorter wave-lengths would seem to be necessary for the calculation of formulæ, but meanwhile the observations are of interest as indicating the separation in the doublets constituting the series

As many as seventeen lines were observed in the spark spectrum by Eder and Valenta, but, with specially pure material, only three lines were found by Crookes,† two of which form the pair at λ2497, while the third has the wave-length 3451·35.

* An Soc Española Fis. y Quim., 15, No 38 (1917).
† Proc Roy Soc., A 86, 36 (1911)

Al Doublets

Principal $1\sigma - m\pi$
$1\sigma = 22933\ 27$

λ, Int	ν	Δν	m	$m\pi_{1,2}$
—3961 540(10*R*)	—25235 60	112 01	(1)	48168 87
—3944 032(10*R*)	— 347 61			280 88
13125 36	7616 79	15 22	(2)	15316 48
13151 65	01 57			331 70
6696 064 (3)	14930 03	5 95	(3)	8003 24
98 734 (3)	924 08			09 19
5557 08 (1*n*)	17990 08	2 82	(4)	4943 19
57 95 (1*n*)	987 26			46 01
*5105 14	19582 7	2 0	(5)	3350 6
* 05 64	580 7			52 6

Sharp $1\pi - m\sigma$
$1\pi_1 = 48168\ 84$, $1\pi_2 = 48280\ 91$

λ, Int	ν	Δν	m	$m\sigma$
3961 540(10*R*)	25235 60	112 01	(1)	22933 27
44 032(10*R*)	347 61			
2660 393(10*R*)	37577 28	112 03	(2)	10591 58
52 484(10*R*)	680 31			
2378 408 (3)	42032 08	112 06	(3)	6136 76
72 084 (3)	144 14			
2263 731 (2)	44161 16	112 09	(4)	4007 67
57 999 (2)	273 25			
*†2204 66 (4)	45344 3		(5	2833 2
2199 64 (1)	447 7			

Al Combinations

λ, Int	ν	ν calc
21166 3	4723 23	$2\pi_1 - 2\sigma$ = 4724 90
21098 2	4738 47	$2\pi_2 - 2\sigma$ = 4740 12
16752 2	5967 76	$2\pi_1 - 3\delta$ = 5969 26
16720 5	5979 07	$2\pi_2 - 3\delta'$ = 5979 99
* 2426 14(4*r*)	41205 2	$1\pi_1 - 3\varphi$ = 41206 3
* 19 56(2*r*)	317 2	$1\pi_2 - 3\varphi$ = 41318 3
* 2312 48(2)	43230 4	$1\pi_1 - 4\pi_1$ = 43225 7
* 2231 20(1*r*)	44804 9	$1\pi_1 - 5\pi_1$ = 44818 3
* 25 70(1*r*)	915 7	$1\pi_2 - 5\pi_2$ = 44928 3

* Kayser and Runge (other lines by Paschen or Grunter)

† Confused with a δ line

‡ This and three following lines are given as arc lines by K R , but Huppers records them only in the spark.

§ Satellites not seen beyond this

Diffuse $1\pi - m\delta$
$1\pi_1 = 48168\ 84$, $1\pi_2 = 48280\ 91$

λ, Int	ν	Δν	m	$m\delta'$, δ
3092 843(6*R*)	32323 36	1 33	(2)	15845 49
92 716(10*R*)	324 69	112 04		844 15
3082 159(10*R*)	32435 40			
2575 411(3*R*)	38817 13	4 49	(3)	9351 71
75 113(10*R*)	821 62	112 07		47 22
2567 997(10*R*)	38929 20			
2373 360(2*R*)	42121 49	4 04	(4)	6047 37
73 132(8*R*)	125 53	112 03		43 31
2367 064(8*R*)	42233 52			
§2269 212(2*R*)	44054 51	2 31	(5)	4114 33
69 093(4*R*)	056 82	112 07		12 09
2263 453(4*R*)	44166 58			
2210 046(2*R*)	45233 78		(6)	2935 96
04 627(2*R*)	344 93			35 06
2174 028(1*R*)	45983 10		(7)	2187 09
68 805(1*R*)	46093 82			85 74
2150 59 (1)	46484 2		(8)	1684 3
45 39 (1)	596 9			
2134 70 (1)	46830 2		(9)	1336 9
29 44 (1)	945 8			
*2123 38 (1)	47079 9		(10)	1091 0
* 18 52 (1)	187 8			

Fundamental $2\delta - m\varphi$
$2\delta = 15844\ 3$

λ	ν	Δν	m	$m\varphi$
11255 5	8882 2		(3)	6962 6
8774 7	11393 3		(4)	4451 5

Unclassified Lines of Al

λ, Int	ν	λ	ν
3066 16 (4)	32604 6	2321 57 (2)	43060 7
64 30 (4)	624 4	‡19 05 (2)	107 9
59 93 (2)	671 0	17 48 (2)	137 1
57 16 (5)	700 6	14 98 (2)	183 7
54 70 (4)	726 9	13 53 (2)	210 7
50 08 (4)	776 6		

Aluminium

Al At wt =27 1, At No =13

An excellent series of measures of the lines constituting the arc spectrum of aluminium was made by Kayser and Runge, and it is still necessary to make use of their determinations of some of the fainter lines Wave-lengths of arc and spark lines on the new scale have been determined over a long range (6929-2129) by R Grunter,* and in the region more refrangible than 3200 by W Huppers † Measures in the region 2500-1850 have also been given for the spark by Eder ‡

The vacuum arc spectrum in the Schumann region has been observed by McLennan, § but no connection of the lines with the established series has been recognised It should be observed that the vacuum arc usually develops spark lines, so that the true arc lines in this region, if any, are not known

Reference has already been made (p 39) to the abnormal arrangement of the satellites, and to the difficulty of representing the diffuse series by a simple formula

The adopted limits are based upon those calculated by Dunz for the sharp series

Ionised Aluminium (Al^{++})

Enhanced lines of aluminium are numerous and well marked, but no series have yet been traced The most recent measures are those of Grunter, which extend from the red to the ultra-violet The spark lines in the Schumann region have been tabulated, and a photograph reproduced, by Lyman ‖

In connection with Kossel and Sommerfeld's "displacement law" (p 74), according to which the ionised elements of the Al sub-group should exhibit triplet series, it should be noted that Popow¶ had previously directed attention to the following triplets, which may represent Al^{+} —

λ vac	ν	Δν
1765 7 (8)	56635	
		122
61 9 (8)	757	
		61
60 0 (8)	818	
1725 0 (10)	57971	
		128
21 2 (9)	58099	
		64
19 3 (9)	163	

The second triplet is quite isolated, but the first occurs as part of a group of five lines, and some doubt is thrown upon its assignment to Al^{+} by the fact that McLennan did not observe the third line in the vacuum arc

Gallium

Ga At wt =69 9, At No =31

Very few lines have been observed in the spectrum of gallium, but it is possible that the records are incomplete in consequence of difficulty in obtaining material for experiment While the spectrum was almost unknown, Rydberg made an

* Zeit f Wiss Phot, **13**, 1 (1914)
† *Ibid.*, **13**, 46
‡ *Ibid.*, **13**, 20, **14**, 137 (1915)
§ Proc Roy Soc, A. **95**, 323 (1919).
‖ "Spectroscopy of the Extreme Ultra-Violet"
¶ Ann d Phys, **45**, 166 (1914).

interesting calculation of the formulæ for the subordinate series by interpolation from the constants for related elements For the limits of the subordinate series he deduced 47390 and 48222, and the calculated positions of some of the lines were not very widely different from those subsequently observed Our knowledge of the series has been extended by Paschen and Meissner,* whose observations have been utilised in the table which follows All the known arc lines are included in the table

Exner and Haschek have recorded nine lines which are special to the spark spectrum in the region λ4172 to λ2450, and other spark lines were recorded in the visible spectrum by the discoverer of gallium, Lecoq de Boisbaudran †

Ga DOUBLETS

PRINCIPAL $1\sigma - m\pi$
$1\sigma = 23591\ 5$

λ, Int	ν	Δν	*m*	$m\pi_{1,2}$
—4172 06 (30*R*)	—23962 3	826 0	(1)	47553 8
—4033 03 (30*R*)	—24788 3			48379 8
*[11940]	[8373]		(2)	[15218]
*[12096]	[8265]			[15326]
6396 89	15628 3	41 1	(3)	7963 2
6413 77	587 2			8004 3
5353 81	18673 1	20 9	(4)	4918 4
59 8	652 2			39 3

DIFFUSE $1\pi - m\delta$
$1\pi_1 = 47553\ 8$, $1\pi_2 = 48379\ 8$

λ, Int.	ν	Δν	*m*	$m\delta'$, δ
2944 18 (5*R*)	33955 4	6 0	(2)	13598 3
43 66 (10*R*)	961 4	826 2		592 4
2874 24 (10*R*)	34781 6			
——	——		(3)	7577 1
2500 18 (2*R*)	39985 1			68 7
2450 10 (2*R*)	40802 7			

SHARP $1\pi - m\sigma$
$1\pi_1 = 47553\ 8$, $1\pi_2 = 48379\ 8$

λ, Int	ν	Δν	*m*	$m\sigma$
4172 06 (30)	23962 3	826 0	(1)	23591 5
4033 03 (30)	24788 3			
2719 66 (3)	36758 5	826 6	(2)	10795 0
2659 84 (2)	37585 1			

COMBINATION

λ	ν	ν *calc*
3020 49 (3)	33097 6	$1\pi_2 - 2\pi_2 = 33054$

* Calculated lines

INDIUM

In At wt =114 8, At No =49

The sharp and diffuse series of indium doublets were identified by Kayser and Runge, and by Rydberg, and the principal series by Paschen and Meissner ‡ The limits adopted for the subordinate series are those determined from the sharp series by Johanson These lead to a limit for the principal series which is almost identical with that calculated independently by Paschen and Meissner (22294 9) As in aluminium, the satellite in the first diffuse pair is abnormally close to the chief line

The wave-lengths, other than for the principal series, are due to Kayser and Runge The infra-red region has not been observed, and the fundamental series

* Ann d Phys , **43**, 1223 (1914)
† Comptes Rendus, **82**, 168 (1876)
‡ Ann d Phys , **43**, 1223 (1914)

In Doublets

Principal $1\sigma - m\pi$
$1\sigma = 22294\ 8$

λ, Int	ν	Δν	m	$m\pi_{1,2}$
—4511 27 (10*R*)	—22160 5	2212 6	(1)	44455 3
—4101 72 (8*R*)	—24373 1			46667 9
			(2)	[14519]
				[14811]
6847 77 (8)	14599 3	111 3	(3)	7695 5
6900 37 (6)	488 0			7806 8
5209 75 (5)	17509 1	56 6	(4)	4785 7
28 27 (4)	452 5			4842 3
5253 97 (3)	19027 9	30 4	(5)	3266 9
62 38 (2)	18997 5			97 3
5017 5 (1)	19924 7	21 8	(6)	2370 1
23 0 (0)	902 9			91 9
4878 8 (0)	20491 1		(7)	1803 7

Sharp $1\pi - m\sigma$
$1\pi_1 = 44455\ 3$, $1\pi_2 = 46667\ 9$

λ, Int	ν	Δν	m	$m\sigma$
4511 27 (10*R*)	22160 5	2212 6	(1)	22294 8
4101 72 (10*R*)	24373 1			
2932 60 (6*R*)	34089 4	2212 4	(2)	10366 0
2753 87 (6*R*)	36301 8			
2601 75 (6*R*)	38424 2	2212 8	(3)	6031 0
2460 06 (6*R*)	40637 0			
2468 01 (4*R*)	40506 2	2211 7	(4)	3949 5
2340 22 (6*R*)	42717 9			
2399 25 (4*R*)	41667 0	2213 6	(5)	2787 8
2278 2 (1*R*)	43880 6			
*2357 6 (1*R*)	42403 1		(6)	2068 8
2241 5 (1*R*)	44599 1			
σ_2				
2218 2 (1*R*)	45068		(7)	1600
2199 9 (1*R*)	45442		(8)	1226

Diffuse $1\pi - m\delta$
$1\pi_1 = 44455\ 3$, $1\pi_2 = 46667\ 9$

λ, In	ν	Δν	m	$m\delta'$, δ
3258 52 (6*R*)	30679 9	23 5	(2)	13775 4
56 03 (10*R*)	703 4	2212 5		751 9
3039 34 (10*R*)	32892 4			
2713 95 (6*R*)	36835 8	49 9	(3)	7619 5
10 28 (10*R*)	885 7	2212 5		7569 6
2560 16 (8*R*)	39048 3			
2522 99 (4*R*)	39623 6	25 6	(4)	4831 8
21 36 (8*R*)	649 2	2212 3		06 1
2389 56 (8*R*)	41835 9			
2430 7 (1*R*)	41127 9	17 3	(5)	3328 3
29 68 (1*R*)	145 2	2210 7		10 1
2306 7 (1*R*)	43338 6			
			(6)	2443 6
2379 66 (1*R*)	42009 9			45 4
2260 5 (1*R*)	44224 3			
δ_2				$m\delta'$
2230 8 (1*R*)	44813		(7)	1855
2211 1 (1*R*)	45212		(8)	1456
2197 4 (1*R*)	45494		(9)	1174
2187 4 (1*R*)	45702		(10)	966
2179 9 (1*R*)	45859		(11)	809

In Combinations

λ, Int	ν	ν *calc*
2720 00 (2*n*)	36753 9	$1\pi_1 - 3\pi_1 = 36759\ 8$
2565 50 (2*n*)	38967 1	$1\pi_2 - 3\pi_1 = 38972\ 4$
2572 62 (2*r*)	38859 3	$1\pi_2 - 3\pi_2 = 38861\ 1$
2666 23 (2)	37495 0	$1\pi_1 - 3\varphi = 37495\ 0$†

* λ possibly in error
† 3φ assumed = 6960 3, which is a probable value

In DOUBLETS—*Continued*

Unclassified Lines of In *			
λ, Int	ν	λ, Int	ν
4108 84 (1*R*)	24330 9	2858 19 (1)	34976 9
3610 50 (1 ?)	27689 1	58 08 (1)	978 2
3261 06 (2 ?)	30656 0	36 90 (3*R*)	35239 4
3186 79 (1)	31429 6	2775 36 (1)	36020 7
3066 30 (1*R*)	32603 1	2470 57 (2 ?)	40464 2
51 19 (1)	764 7		
51 07 (4)	765 9	* All except the last are from Exner and Haschek	
2957 02 (2*R*)	33808 0		

has accordingly not yet been identified As in other elements of this sub-group, nearly all the arc lines have been classified Only one of Kayser and Runge's lines is outstanding, but twelve faint lines given by Exner and Haschek do not appear to be capable of explanation as combinations

The spark spectrum shows some characteristic lines, but possible series have not been investigated Rydberg, however, called attention to two pairs of lines having a separation $\Delta\nu=7926$, according to Hartley and Adeney's wave-lengths The more accurate measures by Exner and Haschek, however, do not confirm the equality of the separations The lines in question are (in I A) —

λ, Int	ν	Δν
3835 0 (3*n*)	26068 3	7920 6
2941 28 (10)	33988 9	
2890 24 (4)	34589 0	7937 4
2350 76 (1)	42526 4	

Measures of the spark spectrum on the international scale have been made by Schulemann,* covering the region λ7455—2264, and giving a large number of lines not recorded by other observers For the above pairs, his values give the separations as 7922 74 and 7937 84

THALLIUM

Tl At wt =204 0, At No =81.

The series spectrum of thallium is well developed, and consists of widely-separated pairs, so that while one component of the first principal pair lies in the green, the other is in the ultra-violet Thallium is remarkable for the easy reversal of most of the series lines

The most complete measures of the arc spectrum are those of Paschen, and Kayser and Runge, whose wave-lengths have been adopted from the red to λ2129. Beyond this, the only published wave-lengths of the series lines are those determined by Cornu,† which are subject to considerable uncertainty A list of wave-lengths from 3229 to 2210 has been given by Huppers,‡ but is too incomplete for our present purpose The series are tabulated as given by Dunz, with the figures corrected to the international system, and a few additional combinations The limits of the sub-

* Zeit f Wiss Phot , **10**, 263 (1912)
† Jour de Phys , (2) **5**, 93 (1886)
‡ Zeit f Wiss Phot , **13**, 74 (1914)

Tl Doublets

PRINCIPAL $1\sigma - m\pi$
$1\sigma = 22786\ 7$

λ, Int	ν	Δν	m	$m\pi_{1,2}$
—5350 46 (10R)	—18684 8	7792 7	(1)	41471 5
—3775 72 (10R)	—26477 5			49264 2
11513 22	8683 3	1001 2	(2)	14103 4
13013 8	7682 1			15104 6
6549 77 (8)	15263 5	372 7	(3)	7523 2
6713 69 (6)	14890 8			7895 9
5527 90 (4)	18085 0	181 6	(4)	4701 7
83 98 (2)	17903 4			4883 3
5109 47 (2)	19566 1	104 3	(5)	3220 6
36 84 (1)	461 8			3324 9
4891 11 (2)	20439 6	63 3	(6)	2347 1
4906 3 (2)	376 3			2410 4
4760 6 (1)	20999 9	34 8	(7)	1786 8
68 5 (1)	965 1			1821 6
4678 1 (3)	21370 2		(8)	1416 5
4617 2 (2)	21652 1		(9)	1134 6
4574 6 (1)	21853 7		(10)	933 0
4547 9 (0)	21982 0		(11)	804 7

SHARP $1\pi - m\sigma$
$1\pi_1 = 41471\ 5$ $1\pi_2 = 49264\ 2$

λ, Int	ν	Δν	m	$m\sigma$
5350 46 (10R)	18684 8	7792 7	(1)	22786 7
3775 72 (10R)	26477 5			
3229 75 (10R)	30953 2	7792 8	(2)	10518 3
2580 14 (8R)	38746 0			
2826 16 (8R)	35373 3	7792 7	(3)	6098 2
2315 93 (6R)	43166 0			
2665 57 (2n)	37504 3	7790 7	(4)	3968 2
2207 06 (4R)	45295 0			
2585 59 (4R)	38664 4	7789 1	(5)	2808 9
2152 01 (1R)	46453 5			
2538 18 (2R)	39386 5		(6)	2085 0
‡2119 1	47174 6			
2507 94 (1R)	39861 3		(7)	1610 2
2098 4	47640 1			
2487 48 (1R)	40189 2		(8)	1282 3
2083 1	47989 9			
2472 57 (1R)	40431 5		(9)	1040 0
2072 3	48240 2			
*2461 93 (1R)	40606 2		(10)	865 3
*2453 79 (1R)	40741 0		(11)	730 5
*2447 51 (1R)	40845 5		(12)	626 0
*2442 16 (1R)	40935 0		(13)	536 5

* More refrangible components not recorded
† Satellites not observed beyond this pair
‡ This and smaller wave-lengths may be much in error

DIFFUSE $1\pi - m\delta$
$1\pi_1 = 41471\ 5$, $1\pi_2 = 49264\ 2$

λ, Int	ν	Δν	m	$m\delta'$, δ
3529 43 (8R)	28325 2	82 0	(2)	13146 2
19 24 (10R)	407 2			064 3
2767 87 (10R)	36118 2	7793 0		
2921 52 (6R)	34218 8	37 5	(3)	7252 8
18 32 (10R)	256 3			15 2
2379 58 (8R)	42011 3	7792 5		
2710 67 (4R)	36880 4	19 6	(4)	4591 6
09 23 (8R)	900 0			71 5
2237 84 (6R)	44672 0	7791 6		
2609 77 (4R)	38306 1	11 5	(5)	3165 8
08 99 (6R)	317 6			53 9
2168 61 (4R)	46098 0	7791 9		
†2552 98 (2R)	39158 1	7 0	(6)	2314 7
52 53 (6R)	165 1			06 4
2129 33 (1R)	46948 1	7790 0		
				$m\delta$
2517 41 (4R)	39711 4		(7)	1760 1
‡2105 0	47491			
2493 91 (2R)	40085 6		(8)	1385 9
2088 7	47861			
2477 49 (1R)	40351 2		(9)	1120 3
2077 2	48126			
2465 46 (1R)	40548 0		(10)	923 5
2069 1	48315			
2456 45 (1R)	40696 9		(11)	774 6
2062 2	48476			
2449 49 (1R)	40812 5		(12)	659 0
2057 2	48594			
2443 92 (1R)	40905 8		(13)	565 7
2053 8	48675			
2439 50 (1R)	40979 6		(14)	491 9

FUNDAMENTAL $2\delta - m\varphi$
$2\delta = 13064\ 3$, $2\delta' = 13146\ 2$

λ	ν	Δν	m	$m\varphi$
16340 3	6118 2	82 5	(3)	6945 8
16123 0	6200 7			
11594 5	8622 4	84 4	(4)	4440 7
11482 2	8706 8			
			(5)	[3077 0]
9170 7	10901 3		(6)	2244 9?

Tl Combinations

Combinations $1\sigma - m\delta$
$1\sigma = 22786\ 7$

λ, Int	ν	ν calc
10292 3	9713 4	$1\sigma - 2\delta = 9722\ 4$
6420 45 (1)	15570 9	$1\sigma - 3\delta = 15571\ 5$
5488 79 (2)	18213 9	$1\sigma - 4\delta = 18215\ 2$
5093 28 (1)	19628 2	$1\sigma - 5\delta = 19632\ 8$

Combinations $m\pi - m\sigma$

λ	ν	ν calc
27889 6	3584 6	$2\pi_1 - 2\sigma = 3585\ 1$
21803 0	4585 3	$2\pi_2 - 2\sigma = 4586\ 3$
12491 8	8003 7	$2\pi_1 - 3\sigma = 8005\ 2$
7 023μ	1423 5	$3\pi_1 - 3\sigma = 1425\ 0$
5 559μ	1798 6	$3\pi_2 - 3\sigma = 1797\ 7$

Combinations $1\pi - m\pi$

λ, Int	ν	ν calc
*3652 95 (1*n*)	27367 3	$1\pi_1 - 2\pi_1 = 27368\ 1$
2945 04 (4*r*)	33945 5	$1\pi_1 - 3\pi_1 = 33948\ 3$
†2719 10 (1)	36766 1	$1\pi_1 - 4\pi_1 = 36769\ 8$
2977 93 (1*r*)	33570 6	$1\pi_1 - 3\pi_2 = 33575\ 6$
†2843 27 (1)	35160 5	$1\pi_2 - 2\pi_1 = 35160\ 8$
2416 70 (1*r*)	41366 1	$1\pi_2 - 3\pi_2 = 41368\ 3$

Combinations $1\pi - m\varphi$

λ, Int	ν	ν calc
2895 41 (4*v*)	34527 3	$1\pi_1 - 3\varphi = 34525\ 7$
2362 08 (2*v*)	42322 7	$1\pi_2 - 3\varphi = 42318\ 4$
2700 2 (2*n*)	37023 3	$1\pi_1 - 4\varphi = 37030\ 8$

Combinations $2\sigma - m\pi$
$2\sigma = 10518\ 3$

λ	ν	ν calc
33393 2	2993 8	$2\sigma - 3\pi_1 = 2995\ 1$
38131 0	2621 8	$2\sigma - 3\pi_2 = 2622\ 4$

Combinations $2\pi - m\delta$

λ	ν	ν calc
51057 9	1958 0	$2\pi_2 - 2\delta' = 1958\ 4$
14592 6	6851 0	$2\pi_1 - 3\delta' = 6850\ 6$
12736 4	7849 4	$2\pi_2 - 3\delta' = 7851\ 8$
10496 4	9524 5	$2\pi_1 - 4\delta' = 9511\ 8$
9512 4	10509 7	$2\pi_2 - 4\delta' = 10513\ 0$
9136 1	10942 6	$2\pi_1 - 5\delta' = 10937\ 6$
8376 1	11935 5	$2\pi_2 - 5\delta' = 11938\ 8$
14515 5	6887 3	$2\pi_1 - 3\delta = 6888\ 2$
10492 5	9528 1	$2\pi_1 - 4\delta = 9531\ 9$

Combinations $3\delta - m\varphi$

λ	ν	ν calc
3 595μ	2781	$3\delta - 4\varphi = 2774\ 5$
3 568μ	2803	$3\delta' - 4\varphi = 2812\ 1$

Unclassified Lines of Tl

λ	ν	λ	ν
7 117μ	1404 7	‡2671 10 (2*v*)	37426 7
3 92865μ	2544 7	2669 95 (1)	37442 8
3 92155	2549 3	2577 67 (1)	38783 1
2 70276?	3698 9	2532 71 (1*n*)	39471 6
2 70237	3699 4	2530 80 (1*n*)	39501 3
2 13979	4672 1	2512 59 (1)	39787 5
2 04858	4880 1	2434 05 (1)	41071 3
1 45978	6848 5	2417 01 (2)	41360 8
1 16907	8551 4		
3230 6 (1)	30945 1		
2210 73 (2*R*)	45219 8		

* Not given by Dunz
† Given by Huppers
‡ This and succeeding lines are given by Huppers, not by Kayser and Runge The first, second, fifth, and seventh are given in spark by Eder and Valenta

ordinate series were calculated by Dunz from the sharp series It will be seen that nearly all the lines are included in the recognised series

The enhanced lines do not appear to have been investigated for series relationships The vacuum-arc and spark spectra in the region λ1908 to λ1477 have been observed by McLennan *

The sharp series is not well represented by most of the ordinary formulæ For wave-numbers on the Rowland system, however, Johanson has obtained a fair agreement by his formula (*see* p 36) with the constants $A = 41469\ 33$, $\mu = 2\ 261774$, $a = 1\ 672006$, $b = -1\ 937964$

* Proc. Roy Soc., A 98, 108 (1920)

CHAPTER XVIII.

ELEMENTS OF GROUPS IV AND V

ELEMENTS OF GROUP IV

There are no published records of the discovery of typical series in the spectra of any of the elements of this group Constant difference groups, however, were found by Kayser and Runge in the spectra of lead and tin which have been verified with remarkable accuracy in Kayser's laboratory by Klein* and Arnolds† respectively In the arc spectrum of lead there are 10 lines differing in wave-number by 10807 43 from 10 other lines, and these, again, by 2831 2 from other more refrangible lines Similarly, for the arc lines of tin there are 10 sets of three lines for which the separations are 5185 43 and 1735 84

In the spectrum of tin Lohuizen‡ has suggested two groups of parallel series, which he has called "translation series" Thus, he gives six series with limits 45307 40, 50494 43, 50926 14, 52330 66, 53507 27, 53924 00, for all of which the terms "mx" are given by $N/(m+1\ 651360-657\ 42\lambda^{-1})^2$, and three series having limits 43825 00, 49012 03, 50748 26, with the variable terms given by $N/(m+1\ 384406+446\ 70\lambda^{-1})^2$ The number of lines in a series ranges from three to five

In germanium (Ge At wt =72 5, At No =32) Paulson finds three triplets with separations of 1416, 903, and two pairs with a separation equal to the sum of these

Constant difference pairs have also been noted by Paulson among the arc lines of titanium, with separations of 71, 64, 779, or 1166 Only a small proportion of the lines of this element are included

As regards the remaining elements of Group IV, carbon and silicon, some unpublished results obtained by the writer are of interest and may be briefly mentioned

Carbon (C At wt =12 0, At No =6) —The arc spectrum of carbon shows only one line, λ2478, in the whole range of spectrum from the extreme red to λ2000 It is possible that there may be other arc lines in the Schumann region, but the spectrum has not been obtained under conditions which permit them to be distinguished as such with certainty Observations in this region have been made by Wolff,§ McLennan,|| and Millikan ¶

In the spark spectrum of carbon, C^+, the writer has established doublet series for which $\Delta\nu=10\ 8$ and which have $4N$ for the series constant as in other series of ionised elements With greater energy, a triplet is developed near λ4647, having $\Delta\nu=13\ 0$, 5 5, this may possibly represent C^{++}, or the second-step ionisation, but it has not yet been possible to prove this by establishing the triplet as a member of a system of series having $9N$ for constant With the greatest energy, as Merton**

* Zeit f Wiss Phot, **12**, 16 (1913).
† *Ibid*, **13**, 313 (1913)
‡ Proc Roy Acad Amsterdam, April, 1912
§ Ann d Phys, **42**, 837 (1913)
|| Proc Roy Soc, A **95**, 272, 327 (1919)
¶ Astrophys Jour, **52**, 59 (1920)
** Proc Roy Soc, A **91**, 498 (1915)

has shown, certain other lines are developed in the carbon spectrum which correspond with lines in the spectra of Wolf-Rayet stars The wave-lengths of the most prominent of these are 5812 and 5801, forming a pair with $\Delta\nu=31\,4$ This may perhaps represent a third-step ionisation, but the evidence for this is not complete

Silicon (Si At wt =28 3, At No =14) —Lockyer has shown that successive spectra are developed in this element as the energy of excitation is increased, and he has designated them Si I , Si II , Si III , and Si IV , the first representing the arc spectrum These observations, however, covered too restricted a range of spectrum for the investigation of series, and have been extended by the writer

Evidence has been obtained that the arc spectrum, Si I , includes a system of triplets, in which $\Delta\nu=146,\ 77$ There is a diffuse triplet, with a normal set of satellites, a normal sharp triplet, certain other triplets not yet classified, and a number of pairs having separations of 146 or 77 Series formulæ have not been calculated, but the lines in question are undoubted arc lines

The spark spectrum, Si II , shows a system of doublets in which $\Delta\nu=60\,0$ The principal, sharp, and diffuse series are well represented in the spectrum under suitable conditions of experiment, and the series constant for them is definitely $4N$ The doublets are therefore to be assigned to ionised silicon, Si^+

Additional triplets associated with that observed in Si III by Lockyer have been obtained, but not yet in sufficient number to allow of the definite calculation of the series constant It is not improbable, however, that the triplets represent the second-step ionisation, for which the constant would be $9N$, and they may be provisionally assigned to Si^{++}

Lockyer's Si IV was represented by a well-known pair in the violet The separation $\Delta\nu$ is 164, and three other pairs with the same separation have now been found in the ultra-violet Further observations in the Schumann region may establish the character of these pairs, but meanwhile it may be supposed possible that they represent the third-step ionisation, Si^{+++}

It should be noted that the separations of the doublets and triplets in the successive spectra of silicon are related to the corresponding separations in carbon in very close proportion to the squares of the atomic weights

These observations of carbon and silicon are of special interest in connection with Kossel and Sommerfeld's displacement law to which reference has already been made (p 74)

Elements of Group V

No series have been identified in any of the elements of this group Constant difference lines, however, were noted by Kayser and Runge in the spectra of arsenic, antimony and bismuth, and in other elements of the group by Paulson In all cases, the constant separations refer to pairs of lines, two or more separations being involved

It is scarcely possible to summarise the data usefully, and reference must be made to the original sources *

In the case of nitrogen, it should be observed that Stark and Hardtke† have obtained a spectrum which they have described as the arc spectrum The more familiar line spectrum thus becomes the probable spark spectrum, N^+ Prior to Hardtke's work, certain lines developed under a more powerful stimulus were

* Kayser's Handbuch, Vol II , and Paulson's papers previously quoted

† Ann d Phys , 56, 363 (1918)

obtained by Lockyer, Baxandall, and Butler, and described as the enhanced lines of nitrogen This spectrum was afterwards described more completely by Fowler,* and should, perhaps, be considered to represent the second-step ionisation, or N^{++}. The matter is of some importance in connection with Kossel and Sommerfeld's suggestive displacement law, and the following particulars of pairs of lines may be quoted —

	λ I A	ν	$\Delta\nu$
Probable principal pair	4097 33 (10) 4103 39 (8)	24399 30 363 22	36 08
Probable diffuse pair	4641 91 (3) 40 65 (10) 34 17 (8)	21536 84 542 70 572 83	5 86 35 99
Possible sharp pair	4867 14 (4) 58 82 (3)	20540 23 575 40	35 17

The measures of the last pair are less satisfactory than those of the first two

* Monthly Notices R A S , 80 692 (1920).

CHAPTER XIX

GROUP VI —OXYGEN, SULPHUR, AND SELENIUM

Our knowledge of the series lines of the elements of this sub-group is due to Runge and Paschen * Each element shows two distinct line spectra, which are well known under the names of the " compound line " and " elementary line " spectra These names were assigned to the oxygen spectra by Schuster,† and were adopted by Kayser for the corresponding spectra of sulphur and selenium The two spectra are developed respectively by uncondensed discharges and condensed discharges of moderate intensity, and the names given by Schuster were based upon the supposition that complex and simplified molecular groupings were involved in the two cases The compound line spectra were distinguished as the " series spectra " of the respective elements by Runge and Paschen

When powerful condensed discharges are employed, a third system of lines is produced in oxygen‡ and sulphur,§ and it would seem convenient, provisionally, to follow the plan adopted by Lockyer in the case of silicon, and to distinguish the compound line, the elementary line and the third line spectra by adding I, II, III to the chemical symbol of the element, as O I, O II, O III, &c In general terms, the three spectra have been described as the arc, spark and super-spark spectra Intermediate stages may be readily obtained by suitable adjustment of the gas pressure, diameter of capillary tube and intensity of discharge

It is only in the first line spectra that series have at present been identified

OXYGEN

O At wt =16 00, At No =8

The compound line, or O I, spectrum of oxygen exhibits a system of narrow triplets, and a system which was at first described as consisting of doublets The latter, however, were only partially resolved, and the separation was only given for one line of the sharp series, namely —

$$\lambda 6046\ 348\ (7) = \nu 16534\ 34$$
$$\lambda 6046\ 120\ (2) = \nu 16534\ 97 \qquad \Delta\nu = 0{\cdot}63$$

Since most other spectra which show triplets also show singlet series, but never doublets, it is possible that the oxygen series in question may really consist of single lines || They have been entered as singlets in the table

The first principal triplet shows separations $\Delta\nu = 3\ 4,\ 2\ 7$, according to the

* Ann d Phys , **61**, 641 (1897) , Astrophys Jour , **8**, 70 (1898)
† Phil Trans , **170**, 41 (1879)
‡ Fowler and Brooksbank, Monthly Not R A S , **77**, 511 (1917)
§ Lockyer, Proc Roy Soc , A **80**, 55 (1907)
|| See also Sommerfeld, Ann d Phys , **63**, 224 (1920) Recent investigations by Dr. Catalán, however, have suggested that the members of this system may be very narrow triplets

measures of Runge and Paschen; the more recent determinations by Meggers and Kiess* are

λ	ν	$\Delta\nu$
7771·928	12863 28	
74 138	859 62	3 66
75 433	857 49	2 13

and the intervals are thus brought into closer accordance with the separations of the triplets of the subordinate series It may be recalled that the principal triplet occurs in the solar spectrum, and has its origin in the solar atmosphere.

The limits given in the tables have been adapted from those calculated for the sharp series by Dunz The fundamental series should be in the infra-red, where observations have not yet been made

Among the unclassified lines of O I are two "inverted" wider triplets, with mean separations 7 7 and 12 6, which Hicks† has suggested may be united with λ5037 of the *D* series in a "new diffuse series," for which he has calculated the limit 22926

A considerable number of lines of O. I have been observed in the ultra-violet by Schniederjost,‡ but their relation to the established series, if any, has not yet been traced The wave-lengths of these lines are included in the table of unclassified lines.

In the spectrum of O II, six pairs of lines, with separation $\Delta\nu$=179 9, have been identified by the writer, but the series arrangement remains to be discovered

O "SINGLETS"

PRINCIPAL $1S$—mP $1S$=33043 3

λ, Int.	ν	m	mP
8446 38	11836 1	(1)	21207 2
4368 30 (10)	22885 8	(2)	10157 5
3692 44 (7)	27074 7	(3)	5968 6

SHARP $1P$—mS $1P$=21207 2

λ, Int	ν	m	mS
— 8446 38	—11836 1	(1)	33043 3
13163 7	7594 7	(2)	13612 5
7254 05 (2)	13781 6	(3)	7425 6
6046 34 (7*d*)	16534 4	(4)	4672 8
5554 94 (6*d*)	17997 0	(5)	3210 2
5299 00 (5)	18866 3	(6)	2340 9
5146 06 (5)	19426 9	(7)	1780 3
5047 70 (2*n*)	19805 5	(8)	1401 7
4979 55 (1*n*)	20076 6	(9)	1130 6

DIFFUSE $1P$—mD $1P$=21207 2

λ, Int.	ν	m	mD
11287 3	8857 2	(2)	12350 0
7002 22 (4)	14277 3	(3)	6929 9
5958 53 (6*d*)	16778 0	(4)	4429 2
5512 71 (5*d*)	18134 9	(5)	3072 3
5275 08 (4)	18951 8	(6)	2255 4
5130 53 (3)	19485 8	(7)	1721 4
5037 16 (2*n*)	19846 9	(8)	1360 3
4972 87 (1*n*)	20103 5	(9)	1103 7

* Scientific Papers, Bureau of Standards, Washington, No 324, p 644 (1918)

† Phil Trans, A, **213**, 368 (1914)

‡ Zeit f Wiss Phot, **2**, 266 (1904).

O Triplets

PRINCIPAL $1s$—mp
$1s = 36069\ 0$

λ, Int	ν	Δν	m	$mp_{1,2,3}$
7771 97 (10)	12863 2	3 4	(1)	23205 8
74 01 (8)	859 8	2 7		209 2
75 68 (6)	857 1			211 9
3947 33 (10)	25326 5	1 2	(2)	10742 5
47 51 (7)	325 3	0 6		743 7
47 61 (4)	324 7			734 3

SHARP $1p$—ms
$1p_1 = 23205\ 8$, $1p_2 = 23209\ 2$, $1p_3 = 23211\ 9$

λ, Int	ν	Δν	m	ms
—7771 97	—12863 2	3 4	(1)	36069 0
— 74 01	— 859 8	2 7		
— 75 68	— 857 1			
11300	8847 3			
294	8852 0		(2)	14358 5
294	8852 0			
6456 07 (9)	15485 0	3 7		
54 55 (7)	488 7	2 0	(3)	7720 8
53 69 (6)	490 7			
5436 83 (8)	18388 0	3 5		
35 78 (6)	391 5	2 1	(4)	4817 9
35 16 (5)	393 6			
5020 13 (5)	19914 3	3 1		
19 34 (4)	917 4	2 2	(5)	3291 9
18 78 (3)	919 6			
4803 00 (4)	20814 5	3 5		
02 20 (3)	818 0	1 7	(6)	2391 6
01 80 (2)	819 7			
4673 70 (3)	21390 4			
72 75 } (3d)	394 7		(7)	1815 7
72 75 }	394 7			
4589 89 (3)	21780 9			
88 98 } (2d)	785 3		(8)	1425 1
88 98 }	785 3			

DIFFUSE $1p$—md
$1p_1 = 23205\ 8$, $1p_2 = 23209\ 2$, $1p_3 = 23211\ 9$

λ, Int	ν	Δν	m	md
[9266 57]	10788 5			
9263 88	791 7		(2)	12417 3
6158 20 (10)	16234 0	3 8		
56 78 (8)	237 8	2 1	(3)	6971 7
55 99 (7)	239 9			
5330 66 (10)	18754 2	3 8		
29 59 (7)	58 0	2 1	(4)	4451 5
28 98 (6)	60 1			
4968 76 (6)	20120 2	3 6		
67 86 (5)	123 8	1 9	(5)	3085 7
67 40 (4)	125 7			
4773 76 (5)	20942 0	3 8		
72 89 (4)	945 8	1 6	(6)	2263 9
72 54 (3)	947 4			
4655 36 (4)	21474 6	3 7		
54 56 (3)	478 3	1 5	(7)	1731 4
54 23 (2)	479 8			
4577 66 (3)	21839 1		(8)	1367 1
76 79 (2d)	843 3			
4523 53	22100 5		9)	1106 1
22 78 (d)	104 1			

O TRIPLETS—*Continued*

Unclassified Lines of O I

(Runge & Paschen)			(Schniederjost)		
λ, Int	ν	Δν	λ Int	λ	λ
6266 85 (1)	15952 6		2897 31 (2*n*)	2672 79 (1)	2352 53 (2)
64 57 (1)	958 4	7 9	95 26 (3)	38 90 (2)	25 26 (3)
61 47 (3)	966 3	12 4	83 82 (4)	07 42 (2)	2299 86 (3)
56 60 (1)	978 7		81 74 (2*n*)	2577 84 (2)	14 55 (2)
5995 48 (4)	16674 6		58 70 (1)	50 55 (1)	2189 92 (2)
92 45 (3)	683 0		2786 07 (1)	04 58 (2)	37 5 (1)
50 60 (5)	800 4		53 37 (1)	2474 37 (2)	12 3 (1)
5410 76 (3)	18476 6	7 4	23 47 (1)	45 97 (3)	
08 59 (4)	484 0	12 7	08 08 (1)	19 56 (3)	
04 87 (3)	496 7				
4233 32	23615 5		*Oxygen Lines in infra red** (Kiess)		
22 78	674 4		λ, Int	ν	Δν
17 09	706 4				
3830 26	26100 5		8233 05 (<1)	12142 83	4 42
25 07	135 9		30 05 (<1)	147 25	12 14
23 56	146 3		21 84 (1)	159 39	
2883 84	34665 9		7952 22 (<1)	12571 66	2 18
			50 84 (1)	573 84	5 15
			47 58 (2)	578 99	
			7481 27 (<1)	13363 04	3 64
			79 23 (<1)	366 68	4 74
			76 58 (1)	371 42	

* Pop Ast, **29**, 19 (1921)

SULPHUR

S At wt =32 07, At No =16

The compound line spectrum of sulphur (S I) is found only in vacuum tube observations Nearly all the lines are included in a system of triplets resembling those of O I, but having a wider separation Some of the earlier members of the series have not yet been observed The limits of *s* and *d* have been adapted from those given by Dunz

It should be noted that the *p* series is not indicated by Dunz, and that the first *p* triplet, which lies in the infra-red and outside the range of the observations, has been calculated from the Rydberg relations Thus, the limit $1p_1$ having been determined from the *d* series, we have

$$20085\ 5 = 1p_1 = N/(1+p_1)^2$$
$$p_1 = 1\ 336781$$
$$N/(2+p_1)^2 = 2p_1 = 9850\ 7$$
$$\text{Observed } p_1(2) = 1s - 2p_1 = 21297\ 0$$

$$1s = 31147\ 7$$
$$1p_1 = 20085\ 5$$

$$\text{Calculated } p_1(1) = 11062\ 2$$

The position thus assigned to $p_1(1)$ depends solely upon the Rydberg formula, and is probably not exact, but it might have been sufficiently near to suggest a combination which would have indicated the necessary correction

S TRIPLETS

PRINCIPAL $1s—mp$
$1s=[31147\ 7]$

λ, Int.	ν	Δν	*m*	$mp_{1,2,3}$
	[11062 2]	17 9	(1)	20085·5
	[044 3]	11 3		103 4
	[033 0]			114 7
4694 18 (10)	21297 0	6 0	(2)	[9850 7]
95 51 (8)	291 0	3 6		[56 7]
96 31 (6)	287 4			[60 3]

SHARP $1p—ms$
$1p_1=20085\ 5$, $1p_2=20103\ 4$, $1p_3=20114\ 7$

λ, Int	ν	Δν	*m*	*ms*
6415 47 (4)	15583 0	17 9	(4)	4502 5
08 11 (3)	600 9	11 3		
03 49 (2)	612 2			
5889 86 (2)	16973 6	18 3	(5)	3111 6
83 52 (2)	991 9	11 4		
79 57 (1)	17003 3			
5614 26 (5)	17806 9	17 8	(6)	2278 9
08 65 (4)	824 7	10 6		
05 30 (3)	835 3			
5449 78 (3)	18344 3	18 2	(7)	1741 1
44 37 (2)	362 5			

Unclassified Lines of S

λ, Int	ν	Δν
7241 7 (2)	13805 1	
6538 60 (1)	15289 6	5 3
36 33 (1)	294 9	
6396 69 (1)	15628 8	4 4
94 89 (1)	633 2	

DIFFUSE $1p—md$
$1p_1=20085\ 5$, $1p_2=20103\ 4$, $1p_3=20114\ 7$.

λ, Int	ν	Δν	*m*	*md*
6757 16 (7)	14795 1	18 2	(4)	5290 2
48 83 (6)	813 3	11 3		
43 69 (5)	824 6			
6052 75 (7)	16516 9	18 4	(5)	3568 3
46 01 (6)	535 3	11 1		
41 95 (5)	546 4			
5706 22 (8)	17519 9	18 0	(6)	2565 7
00 36 (7)	537 9	10 9		
5696 80 (6)	548 8			
5506 98 (5)	18153 7	17 9	(7)	1931 8
01 56 (3)	171 6	11 3		
5498 16 (3)	182 9			
5380 99 (4)	18578 8	18 0	(8)	1506 8
75 78 (3)	596 8	10 9		
72 62 (2)	607 7			
5295 69 (4)	18878 0	17 8	(9)	1207 8
90 72 (4)	895 8	10 7		
87 71 (2)	906 5			

Unclassified Lines of S—*continued*

λ, Int	ν	Δν
6175 80 (1)	16187 8	5 8
73 56 (1)	193 6	
*5279 02 (6)	18937 6	1 4
78 64 (5)	939 0	1 8
78 14 (3)	40 8	

* Compare with isolated triple group in Se

SELENIUM

Se. At. wt =79 2, At No =34

The compound line spectrum of selenium (Se I) generally resembles the corresponding spectrum of sulphur In the diffuse series of triplets, however, many of the brighter components are accompanied by fainter lines or satellites which are not arranged in the normal way. The first line of a triplet appears to

Se TRIPLETS

PRINCIPAL $1s—mp$.
$1s=[30699\ 0]$

λ, Int	ν	Δν	m	$mp_{1,2,3}$
	[11431 3]		(1)	19267 7
	[327 6]			371 4
	[282 8]			416 2
4731 04(10)	21131 9	36 7	(2)	[9567 1]
39 28(9)	095 2	14 4		[9603 8]
42 58(8)	080 8			[9618 2]

SHARP $1p—ms$
$1p_1=19267\ 7$, $1p_2=19371\ 4$, $1p_3=19416\ 2$

λ, Int	ν	Δν	m	ms
6746 42(6)	14818 6	103 7		
6699 55(6)	922 3	44 8	(4)	4449 1
79 49(5)	967 1			
6177 66(3)	16182 9	103 7		
38 30(2)	286 6	44 1	(5)	3085 0
21 74(2)	330 7			
5878 66(2)	17006 0	104 0		
42 88(2)	110 0	44 7	(6)	2261 5
27 68(1)	154 7			
5700 10(3)	17538 7	103 3		
5666 73(3)	642 0	44 7	(7)	1729 3
52 40(3)	686 7			

† *Unclassified Lines of* Se I

λ, Int	ν	Δν
6831 04(5)	14635 0	
6701 06(1)	14918 9	
6283 33(2)	15910 8	
6135 31(1)	16294 6	
5866 31(2)	17041 8	
5374 08(10)	18602 7	14 6
5369 85(10)	18617 3	15 5
5365 40 (8)	18632 8	

* Lines tabulated for diffuse series by Dunz

† Some of the lines tabulated under diffuse series should possibly be included under this head

DIFFUSE $1p—md$
$1p_1=19267\ 7$, $1p_2=19371\ 4$, $1p_3=19416\ 2$

λ, Int.	ν	Δν	m	md
7061 88(5)	14156 7*		(4)	5112 5
		103 5		
7013 98(3)	14253 3			
10 58(3)	260 2*			
		40 6		
6990 71($4d^2$)	14300 8*			
6325 60(6)	15804 4		(5)	3462 1
25 2 (1)	805 4*			
		103 7		
6284 30(3)	15908 3			
83 98(1)	909 1*			
		45 3		
6269 07(3)	15946 9			
66 15(4)	954 4*			
5961 86(5)	16768 7		(6)	2498 2
61 5 (1)	769 7*			
		103 5		
5925 09(1)	16872 7			
24 91(4)	873 2*			
		44 7		
5909 27(2)	16917 9*			
06 88(2)	924 7			
5753 30(7)	17376 5		(7)	1887 9
52 09(2)	380 2*			
		103 4		
5718 3 (1)	17482 9			
18 06(7)	483 6*			
		44 2		
5704 96(3)	17523 8			
03 64(4)	527 8*			
5617 83(5)	17795 5*		(8)	1472 2
5528 42(4)	18083 3*		(9)	1184 3
		103 9		
5496 85(3)	18187 2*			
5464 61(3)	18294 5		(10)	973 2

have a satellite on the more refrangible side, while the second has a satellite on the less refrangible side, the third line in three of the triplets also has a companion of nearly the same brightness as itself

The normal triplet separations of the sharp series are found in the diffuse series, as shown in the table, but a satisfactory interpretation of the relationships of the remaining components has not been reached The observations of $d(4)$ may be considered incomplete, as are also those of $d(8)$, $d(9)$, and $d(10)$ Those of $d_1(5)$, $d_1(6)$, and $d_1(7)$ suggest that in the first member of the triplet the satellite occupies the normal position, while the chief component is abnormally displaced to the red A similar abnormal displacement is shown by $d_2(5)$, but $d_2(6)$ and $d_2(7)$ show the chief line in the normal position and the satellite displaced to the red The third member in $d(5)$ and $d(7)$ has its companion on the red side, but in $d_2(6)$ the companion is on the violet side There is no very marked regularity in the separations of the chief lines and their companions

The limits of s and d have been adopted from Dunz, with a small correction for the change to the international scale The limit of the principal series has been calculated as in the case of sulphur

The vacuum arc spectrum of selenium in the region $\lambda 2296 - \lambda 1432$ has been observed by McLennan *

Other Elements of Group VI

Constant difference pairs have been noted by Paulson in molybdenum and tungsten, but no regular series have been recognised Some of the spectra are extremely complicated

* Proc Roy Soc, A 98, 113 (1920).

CHAPTER XX.

ELEMENTS OF GROUPS VII AND VIII

Elements of Group VII —Little progress has been made in the analysis of the spectra of the elements of this group

Measures of fluorine of sufficient accuracy do not extend over a large range, and further investigations are much to be desired There are some narrow triplets in the spectrum, which are produced under experimental conditions suggesting that they may belong to the ionised atoms

Chlorine, according to Paulson, shows a few triplets with $\Delta\nu$=about 67, 41, and some pairs with one or other of these separations, or their sum The proper classification of the lines as arc or enhanced lines calls for further experimental investigation

Paulson has found numerous constant difference pairs in bromine and iodine

The arc spectrum of manganese, as shown by Kayser and Runge, appears to include a system of triplets, of which they recognised five members The wavelengths given below are from an extensive investigation of the manganese arc spectrum by Fuchs * The members of the first diffuse triplet are involved in groups of lines, and it is doubtful which of the components should be taken Several are entered in the table, and the $\Delta\nu$ correspond with the lines marked with an asterisk The entire spectrum contains many hundreds of lines, and the series call for further investigation

A few constant difference pairs, and two narrow triplets with separations 14 2 and 8 7 have been noted by Paulson

Mn TRIPLETS

SHARP $1p$—ms $1p_1$=41224 4, $1p_2$=41398 1, $1p_3$=41527 2					DIFFUSE $1p$—md $1p_1$=41224 4, $1p_2$=41398 1, $1p_3$=41527 2				
λ, Int	ν	Δν	m	ms	λ, Int	ν	Δν	m	md
4823 52 (10)	20726 0	173 7	(2)	20498 4	3570 10($4R$)	28002 4*		(2)	13222 4
4783 43 (8)	20899 7	129 1			3569 80($8R$)	28004 8			
4754 05 (10)	21028 8				3569 50($6R$)	28007 1			
							173 1		
					3548 17($4R$)	28175 5*			
3178 51 ($8n$)	31452 2	173 7	(3)	9772 2	3548 02($4R$)	28176 7			
3161 06 (4)	31625 9	129 2					129 0		
3148 19 (4)	31755 1				3532 11($5R$)	28303 6			
					3532 00($5R$)	28304 5*			
					3531 84($4R$)	28305 8			
					2940 40($6n$)	33999 0	172 2	(3)	7226 6
					2925 59($6n$)	34171 2	128 6		
					2914 62($8n$)	34299 8			
					2726 15($4n$)	36670 9	173 1	(4)	4554 4
					2713 35($3n$)	36844 0	127 6		
					2703 98($3n$)	36971 6			

Elements of Group VIII.—No series have been detected in any of the elements of this group, but Paulson has found many constant difference groups, the details of which are too extensive for quotation.

* Zeit f. Wiss Phot, **14**, 239, 263 (1915).

CHAPTER XXI

THE INERT GASES

In addition to helium this group of elements includes neon, argon, krypton, xenon and niton (radium emanation) The spectra are very complex, and it is only in the case of neon that series arrangements have been disentangled In argon, krypton and xenon, however, it has been found possible to arrange many of the lines in groups showing constant differences of wave-number

The spectra of neon, argon, krypton and xenon have been discussed at great length by Hicks,* following his own special methods, but the results cannot be briefly summarised

NEON

Ne At wt = 20 2, At No = 10

The first extensive measures of the lines of neon were made by Baly,† who observed more than 800 lines in the region λ 7000 to λ 3500 Accurate measures of the lines in the less refrangible part of the spectrum have since been made by Meissner,‡ and also of many lines in this region by Burns, Meggers and Merrill,§ many of which are interferometer determinations Several hundreds of lines have also lately been accurately measured by Paschen

Watson‖ was the first to note that many of the strong lines of neon could be arranged in groups of three or four, having constant wave-number separations These are exhibited with remarkable accuracy by the Washington measures Fifteen groups of such lines were found, of which seven are complete quadruplets, five lack the second member, one lacks the third, and in two the second and fourth members are wanting Three examples may be quoted

λ, Int.	ν_{1-4}	$\Delta\nu$
8082 45 (3)	12369 09	
		1070 06
7438 902 (6)	13439 149	
		359 36
7245 167 (8)	13798 507	
		417 45
7032 413 (9)	14215 957	
7024 049 (3)	14232 885	
		1070 073
6532 883 (4)	15302 958	
		359 358
6382 991 (8)	15662 316	
		417 449
6217 280 (4)	16079 765	
6717 043 (5)	14883 402	
		1070 079
6266 495 (7)	15953 481	
		359 39
6128 44 (3)	16312 87	
		417 41
5975 534 (4)	16730 282	

Two sets of apparent doublet series were traced by Rossi¶ with separation about

* Phil Trans, A **220**, 335-468 (1920)
† Phil Trans, A **202**, 183 (1904)
‡ Ann d Phys, **51**, 115 (1916), **58**, 333 (1919) Phys Zeit, **17**, 549 (1916).
§ Scientific Papers, Bureau of Standards, Washington, No 329 (1918)
‖ Astrophys Jour, **38**, 399 (1911)
¶ Phil Mag, **26**, 981 (1913).

167 and converging to the same limits near 24105 and 24272 Several additional series were afterwards recognised by Meissner. All these are included in a masterly analysis of the neon spectrum which has been set forth by Paschen in two recent papers * The spectrum differs from those which have previously been described in having an extraordinarily large number of series Thus, Paschen finds four series of s terms, ten of p terms, and twelve of d terms † The values of the first terms, with Paschen's notation, are as follows ·

s terms	p terms	d terms
$1\ 5s_2 = 38040\ 731$	$2p_1 = 20958\ 718$	$3s_1' = 11493\ 777$
$1\ 5s_3 = 39110\ 808$	$2p_2 = 22891\ 003$	$3s_1'' = 11509\ 498$
$1\ 5s_4 = 39470\ 160$	$2p_3 = 23012\ 015$	$3s_1''' = 11519\ 257$
$1\ 5s_5 = 39887\ 610$	$2p_4 = 23070\ 944$	$3s_1'''' = 11520\ 818$
$*1\ 5s_2 - 1\ 5s_3 = 1070\ 077$	$2p_5 = 23157\ 342$	$3d_1' = 12228\ 051$
$1\ 5s_4 - 1\ 5s_3 = 359\ 352$	$2p_6 = 23613\ 586$	$3d_1'' = 12229\ 816$
$1\cdot5s_5 - 1\ 5s_4 = 417\ 450$	$2p_7 = 23807\ 852$	$3d_2 = 12292\ 853$
	$2p_8 = 24105\ 229$	$3d_3 = 12322\ 259$
	$2p_9 = 24272\ 411$	$3d_4 = 12337\ 323$
	$2p_{10} = 25671\ 654$	$3d_4' = 12339\ 151$
		$3d_5 = 12405\ 233$
		$3d_6 = 12419\ 875$

* These are the constant difference values previously noted

The possible number of combinations is thus very large, but not all of them appear in the spectrum For example, of the 40 possible principal series $1\ 5s - mp$, 30 are actually observed, and there are similarly 30 sharp series, of the possible 120 series of diffuse type, 72 have been identified

A large number of these series were found to be represented with remarkable accuracy by the Ritz formula namely the 72 series

$$\left.\begin{matrix}2p_4\\2p_6\\2p_8\\2p_9\end{matrix}\right\} - md_1' \qquad \left.\begin{matrix}2p_2\\2p_{4\text{-}10}\end{matrix}\right\} - md_3 \qquad \left.\begin{matrix}2p_2\\2p_5\\2p_7\\2p_{10}\end{matrix}\right\} - md_6 \qquad \left.\begin{matrix}1\ 5s_2\\1\ 5s_4\\1\ 5s_5\end{matrix}\right\} - mp_6$$

$$\left.\begin{matrix}2p_4\\2p_{6\ 9}\end{matrix}\right\} - md_4 \qquad 1\ 5s_{2\text{-}5} \quad - mp_7$$

$$\left.\begin{matrix}2p_{1\text{-}8}\\2p_{10}\end{matrix}\right\} - ms_4$$

$$\left.\begin{matrix}2p_4\\2p_5\\2p_{7\text{-}10}\end{matrix}\right\} - md_1'' \qquad 2p_9 \quad - md_4' \qquad \left.\begin{matrix}1\ 5s_2\\1\ 5s_4\\1\ 5s_5\end{matrix}\right\} - mp_8$$

$$\left.\begin{matrix}2p_{2\text{-}4}\\2p_6\\2p_8\\2p_{10}\end{matrix}\right\} - md_5 \qquad \left.\begin{matrix}2p_2\\2p_{4\text{-}10}\end{matrix}\right\} - ms_5$$

$$2p_{1\text{-}10} \quad - md_2 \qquad 1\ 5s_5 \quad - mp_9$$

Owing to the inter-relations between these series, it is sufficient to calculate one limit The one selected by Paschen was $1\ 5s_5$, and the adopted value was the mean from the four series $1\ 5s_5 - mp_{6\text{-}9}$ The terms $2p_{6\text{-}9}$ thus became known, and it was then possible to calculate md_1', md_1'', md_2, md_3, md_4, md_4', md_5, md_6, ms_4, ms_5, $1\ 5s_2$, $1\cdot5s_3$ Then from md_2, &c , the remaining $2p$ terms were found , namely

*Ann d Phys , **60**, 405 (1919) , **68**, 201 (1920)

† In the first paper, four series terms designated s_1', s_1'', s_1''', s_1'''' were considered to be of s type, but in the second paper these are classed as of d type

$2p_{1,2,3,4,5,10}$ Thus, all the limits and terms of the above series could be determined, namely:

$2p_{1\,5}$	$2p_{6\text{-}9}$	$2p_{10}$	$1\,5s_2$	$1\,5s_3$	$1\,5s_{4,5}$	$3d_1'$	$3d_1''$	$3d_{2\text{-}4}$	$3d_4'$	$3d_{5,6}$
	$3p_{6\text{-}9}$				$2\,5s_{4,5}$	$4d_1'$	$4d_1''$	$4d_{2\text{-}4}$	$4d_4'$	$4d_{5,6}$
	$4p_{6\text{-}9}$				$3\,5s_{4,5}$	$5d_1'$	$5d_1''$	$5d_{2\text{-}4}$	$5d_4'$	$5d_{5,6}$

These terms being known, the following combination lines were found to exist

$2p_{1\,8,10}-1\,5s_2$	$1\,5s_{2,4}-2p_1$	$1\,5s_{2,4}-2p_3$	$1\,5s_{2\text{-}5}-2p_5$
$2p_{2,5,7,10}-1\,5s_3$	$1\,5s_{2\text{-}5}-2p_2$	$1\,5s_{2,4,5}-2p_4$	$1\,5s_{2\text{-}5}-2p_{10}$

The lines thus indicated were the first lines of additional series, and it was natural to take the limits of such series as $2p_{1\text{-}8,10}$, $1\,5s_{2,4}$, &c When this was done, however, the terms of the new series did not follow any known type of series formula With limits calculated independently, from the actual lines, the series were nevertheless of the ordinary type Two alternatives were therefore open (1) to preserve the limits indicated by the combination principle and to assert the series to be abnormal, (2) to calculate the limits from the Ritz formula and to abandon or modify the combination principle In his first paper Paschen adopted the first alternative and proposed new types of formulæ, in the second paper he adopted the second alternative

Besides the above, the following 28 series were also found —

$A_{1\text{-}8,10}$	$-ms_1'$	$A_{4,6,8,9}$	$-ms_1'''$
$A_{2,4\text{-}10}$	$-ms_1''$	$A_{2,4\text{-}8,10}$	$-ms_1''''$

The terms ms_1', ms_1'', ms_1''', ms_1'''' are new and do not arise from the combination principle There appears, therefore, to be no obvious reason why A should be identified with any of the known terms Paschen, however, called it $2p$ and again got "abnormal" series The only justification for this procedure seems to be that the limits calculated by the Ritz formula were identical with those of some of the series for which the above alternatives were open As before, the second alternative was finally adopted

The main points in the above arguments may be illustrated by the following numerical calculations —

$1\,5s_5=39887\,61\pm0\,05$ (from the 4 Ritz type series $1\,5s_5-mp_{6\text{-}9}$)

First lines of $1\,5s_5-mp_{6,7,8}$ are $\nu=16274\,02$, $16079\,76$, $15782\,38$

$2p_6=23613\,59$, $2p_7=23807\,85$, $2p_8=24105\,23$

First lines of $1\,5s_2-mp_{6,7,8}$ are $\nu=14427\,14$, $14232\,88$, $13935\,51$

$$1\,5s_2=\text{mean of}\begin{cases}23613\,59+14427\,14=38040\,73\\23807\,85+14232\,88=\quad 73\\24105\,23+13935\,51=\quad 74\end{cases}=38040\,73$$

First lines of $1\,5s_4-mp_{6,7,8}$ are $15856\,57$, $15662\,31$, $15364\,93$

$$1\,5s_4=\text{mean of}\begin{cases}23613\,59+15856\,57=39470\,16\\23807\,85+15662\,31=\quad 16\\24105\,23+15364\,93=\quad 16\end{cases}=39470\,16$$

First lines of $2p_4-ms_{4,5}$ are $-16399\,22$, $-16816\,67$

$$2p_4=\text{mean of}\begin{cases}39470\,16-16399\,22=23070\,94\\39887\,61-16816\,67=\quad 94\end{cases}=23070\,94$$

If there be a combination line $1\,5s_2-2p_4$, its wave-number should be $\nu=38040\,73-23070\,94=14969\,79$

There is a line in this position, and it is the first member of the series —

14969 79
27819 95
32490 07
34708 57
35939 3

This series is accordingly designated $1\,5s_2-mp_4$ where $1\,5s_2=38040\,73$ In this form, however, the series is abnormal, and in his first paper Paschen represented it by the formula

$$\nu=38040\,73-\frac{109694\,8^*}{\left(m-0\,0232537+\frac{0\,0746753}{m}+0\,0612291e^{m/2}\right)^2}$$

If the entire Ritz formula for the series be calculated, however, the limit being regarded as unknown, the limit is found to be 38821 10, and the series is well represented The relative accuracy of the two formulæ is indicated by the following residuals $O-C$

m		2	3	4	5	6
$\Delta\nu$	(Paschen)	+0 01	0 00	+5 83	0 00	−3 50
$\Delta\nu$	(Ritz)	0 00	−0 12	−0 12	+0 21	−3 12

When the Ritz limit 38821 10 is adopted, the values of the terms for the above lines are 23851 31, 11001 15, 6331 03, &c , and these naturally follow the Ritz formula If, however, the limit $1\,5s_2$ (=38040 73) be adopted, then, since 38821 10 =38040 73+780 37, these terms would be decreased by 780 37, and would become 23070 94, 10220 78, 5550 66, &c These do not obey the Ritz formula, and in order to make them do so they must be increased by 780 37 Paschen actually adopts $1\,5s_2$ for the limit, and the terms mp_4 are calculated accordingly , for comparison with the Ritz formula, he then uses terms "(mp_4) reduced," which are equivalent to $mp_4+780\,37$ And similarly for the other series of this character

Altogether, there are 48 series with the limits thus displaced by about 780 units, 2 with displacements of about 730, 4 with 763, 2 with 40, and 4 with displacements of 10 units That is, the limits calculated by the Ritz formula differ by these amounts from those indicated by the combinations which give the first lines of the series The significance of these displacements is not yet understood

Besides these 60 " abnormal " series, there are the 72 normal series previously indicated

* This is Paschen's value for the series constant of neon calculated in accordance with the quantum theory.

The following table shows the wave-lengths, intensities, and classification of some of the well-known strong lines of neon, together with the Zeeman effects when known —

λ	Int	Series	Zeeman type
6717 042	2	$1\ 5s_2—2p_5$	Normal triplet
6266 495	15	$1\ 5s_3—2p_6$	" "
5852 488	50	$1\ 5s_2—2p_1$	" "
6074 337	10	$1\ 5s_4—2p_3$	3/2 Normal triplet
5400 556	50	$1\ 5s_4—2p_1$	3/2 " "
6506 527	15	$1\ 5s_4—2p_8$	
6402 246	20	$1\ 5s_5—2p_9$	
6334 428	10	$1\ 5s_5—2p_8$	
5975 534	12	$1\ 5s_5—2p_5$	

A second spectrum of neon, developed under the action of a condensed discharge, has been observed by Merton,* but no investigations of series in this spectrum have been published

Argon

A At wt =39 9, At No =18

Two spectra are given by argon That obtained with the uncondensed discharge has its strongest lines in the less refrangible regions, and is called the " red spectrum," while that developed by the condensed discharge has its brightest lines in the blue, and is called the " blue spectrum "

Rydberg† found that most of the lines between λ4702 and λ2967 in the red spectrum could be arranged in quadruplets having constant separations, and the same arrangement was afterwards found by Paulson‡ to extend to the less refrangible parts of the spectrum If the first line of each quadruplet be designated A, and succeeding ones B, C, D, it results that

$B=A+$ 846 47	$\Delta_1=846\ 47$ §
$C=A+1649\ 68$	$\Delta_2=803\ 21$
$D=A+2256\ 71$	$\Delta_3=607\ 03$

Some of the " quadruplets " are incomplete, exhibiting only two or three members, and no simple regularity of intensities is evident Neither Rydberg nor Kayser and Runge succeeded in tracing anything of the nature of the typical series spectra

* Proc Roy Soc, A **89**, 447 (1914)
† Astrophys Jour, **6**, 338 (1897)
‡ Phys Zeit, **15**, 831 (1914)
§ More accurate determinations of the wave-lengths and separations have since been published by Meggers (Scientific Papers, Bureau of Standards, Washington, No 414, 1921)

Groups of lines in the blue spectrum, some of them incomplete, were also found by Paulson * These may be represented by the following expressions —

$B=A+$ 844 49	$\Delta_1=$ 844 49
$C=A+2455$ 82	$\Delta_2=1611$ 33
$D=A+2605$ 37	$\Delta_3=$ 149 55
$E=A+2759$ 34	$\Delta_4=$ 153 97

There are also numerous pairs of lines in the spectrum having the differences Δ_1, Δ_2, Δ_3, Δ_4, or $C-A$, $D-A$, &c

A preliminary analysis of the spectrum of argon, following the methods adopted by Paschen for neon, has been made by Nissen †

Krypton

Kr At wt =82 9, At No =36

The original determinations of krypton lines by Baly ‡ have recently been supplemented by some very accurate measurements in the region λ8929-6421 made by Merrill at Washington § A first inspection of the latter measures revealed three additional pairs of the type discovered by Paulson || The eight pairs are given by Merrill as follows —

λ, Int	Δν	λ, Int	Δν
8776 73 (3)	945 06	5870 90 (10)	944 96
8104 33 (7)		5562 23 (6)	
8298 07 (6)	945 00	4502 39 (9)	945 06
7694 53 (8)		4318 58 (8)	
8190 02 (6)	944 97	4463 71 (10)	944 95
7601 55 (20)		4283 01 (4)	
5879 84 (1)	944 99	4453 95 (10)	945 04
5570 28 (10)		4273 99 (10)	

Paulson has also indicated five pairs having a mean separation $\Delta\nu$ of 4732 9

Krypton exhibits two spectra, one produced without condenser in the discharge circuit, and a second when the condenser is introduced The above lines occur in the condensed discharge

Xenon

Xe At wt =130 2, At No =54

The sources of data for xenon are the tables of Baly and Merrill, the latter extending from λ9163 to λ5823

The strongest lines in the red end are 8231 62 and 8280 08, which are believed to be good standards of wave-length in the extreme red

* Astrophys Jour, **41** 75 (1915)
† Phys. Zeit., **21**, 25 (1920)
‡ Phil Trans, A **202**, 183 (1904)
§ Sc Papers, No 345 (1919)
|| Ann d Phys, **45**, 428 (1914)

Paulson* has drawn attention to four "triplets," having separations $\Delta\nu$ of about 3685 and 760 The intensities in these groups, however, show no regularity, and three of the triplets have the wider separation on the more refrangible side

An interesting feature of the spectra of neon, argon, krypton and xenon has been noted by Merrill, namely, the tendency of the lines to form large groups occurring in positions which are apparently related to the atomic weights Merrill photographed the spectra with small dispersion, and the displacement of the groups to the red with increase of atomic weight is thus very clearly indicated Thus, there are groups beginning at λ 5850 in Ne, λ6970 in A, λ7590 in Kr, and λ8230 in Xe. There are comparatively blank spaces on the more refrangible sides of each of these groups Correspondence between individual lines of the different elements, however, is not clear

NITON (Radium Emanation)

Nt. At wt =222 4, At No =86.

The spectrum of the radium emanation was first studied by Ramsay, and afterwards more completely by Rutherford and Royds,† and again by Royds ‡ Wavelengths extending from 6079 to 3005 are thus available,§ but there is no record of any attempt to trace regularity in the arrangement of the lines.

* Astrophys Jour 40, 307 (1914)

† Phil Mag, 16, 313 (1908)

‡ Proc Roy Soc, A 82 22 (1908) Phil Mag, 17, 202 (1909).

§ A further investigation of this spectrum over the range $\lambda\lambda$3982 to 7450 has since been made by Nyswander, Lind, and Moore (Astrophys Jour, 54, 285, 1921).

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DESCRIPTION OF PLATES.

PLATE I.

(1) Arc spectrum of sodium, showing principal, sharp and diffuse series (Quartz spectrograph)

(2) Arc spectrum of lithium, showing principal, sharp and diffuse series (Quartz spectrograph)

(3) The sharp and diffuse series of sodium, with components resolved The principal pair, $\lambda\lambda$5896, 5890, is reversed (Glass spectrograph)

PLATE II

The arc spectra of cadmium, zinc, and magnesium (quartz spectrograph) The triplets of the diffuse and sharp series are marked There is an impurity of zinc in the cadmium spectrum, and of cadmium in the spectrum of zinc The series marked "D" in the spectrum of magnesium is the Rydberg singlet series The line λ2852 is the first principal line of the magnesium singlet system The lines marked at $\lambda\lambda$ 3261, 3076, and 4571, are the "resonance lines" ($1S—1p_1$) of Cd, Zn, and Mg respectively

PLATE III

(*a*) Corresponding sharp triplets of Zn, Cd, and Hg, showing relative positions in the spectrum, and the relative separations

(*b*) A fundamental triplet of barium showing the diffuse character of the lines in the arc in air (lower spectrum), and the presence of satellites in the electric-furnace spectrum at low pressure (A S King, Mt Wilson Observatory)

(*c*) A sharp and a diffuse triplet of calcium compared The fundamental triplet shown on the plate has separations corresponding with those of the satellites of the first diffuse triplet, which lies in the infra-red

PLATE IV

Arc and spark spectra of the alkaline-earth metals In each case the arc is below and the spark above Typical series lines are marked The reduced intensities of the characteristic arc lines, and the enhancement of the spark lines in the spark spectrum are clearly shown The increased separations of the arc triplets, and of the enhanced doublets, with increase of atomic weight should be noted, and also the displacement of corresponding lines towards the red The shorter lines in the spark spectra are due to nitrogen and oxygen (Thorp-grating spectrograph)

PLATE V

(1) The spectrum of helium between λ3188 and λ7066, showing the arrangement of the lines in six series (The two associated fundamental series are in the infra-red)

(2) The upper spectrum is that of helium with an ordinary uncondensed discharge, and the lower that obtained with a strong condensed discharge The latter shows the line λ4686 of He^+ very strongly, while the ordinary lines tend to disappear

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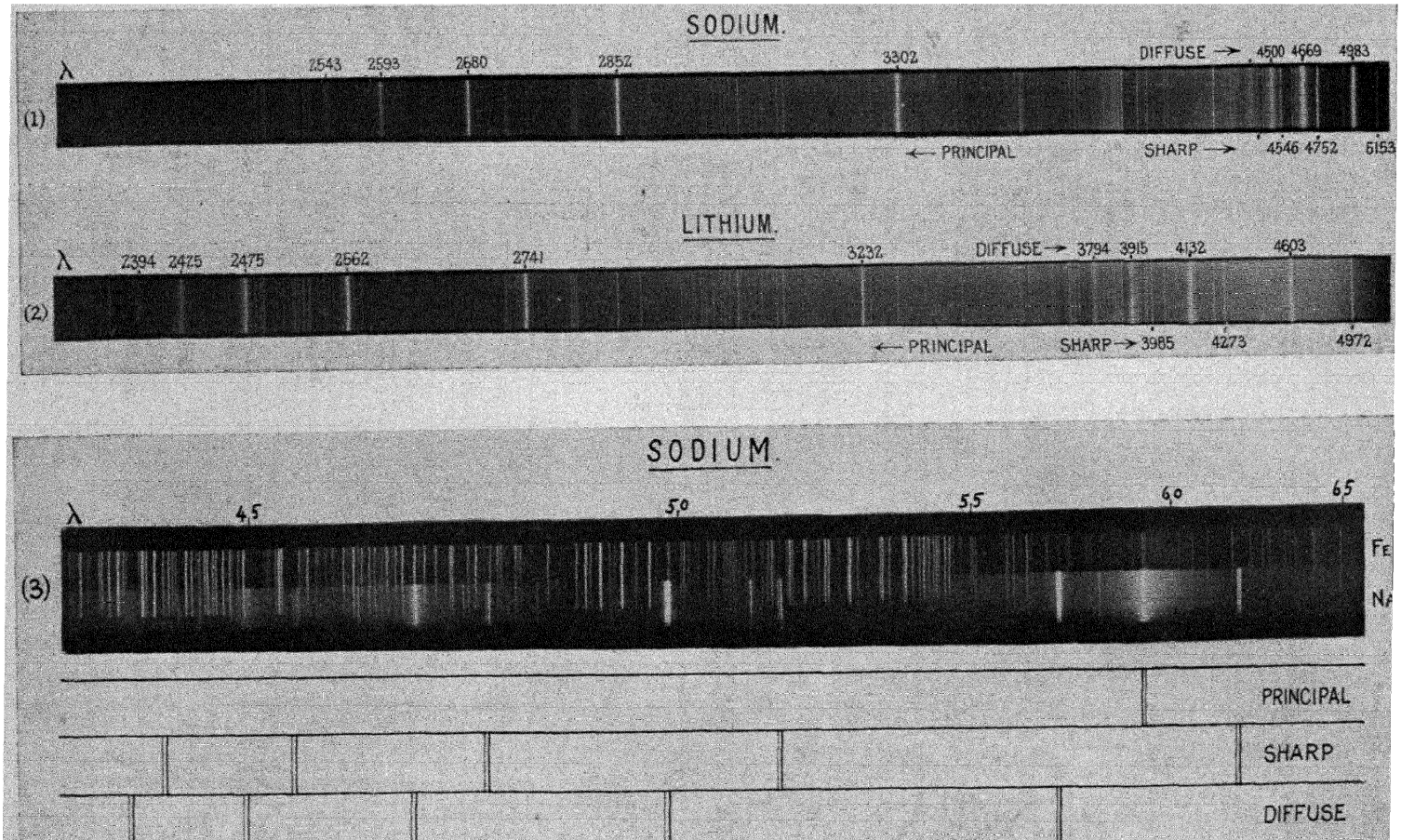


PLATE I — ARC SPECTRA OF SODIUM AND LITHIUM SHOWING THE CHIEF SERIES

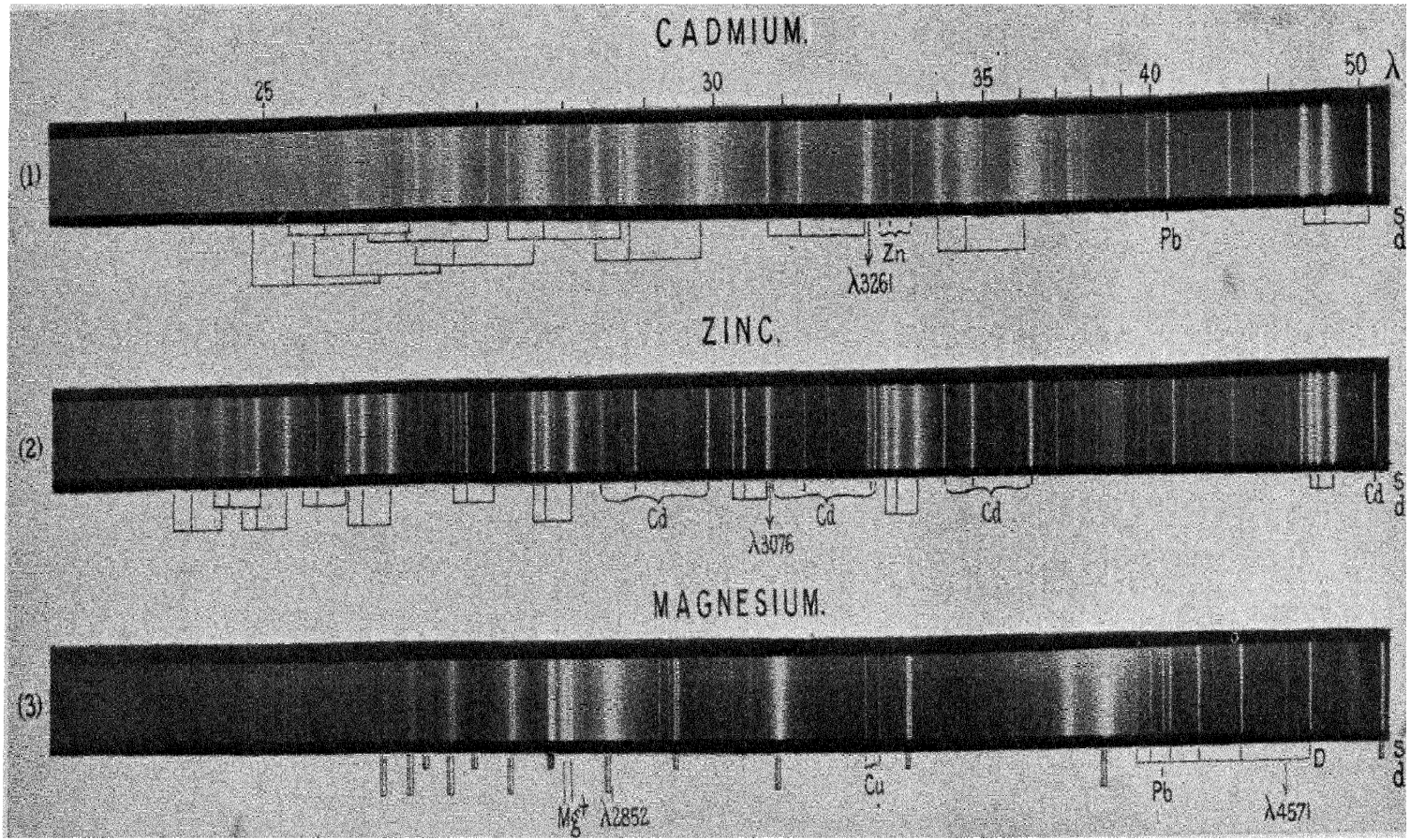
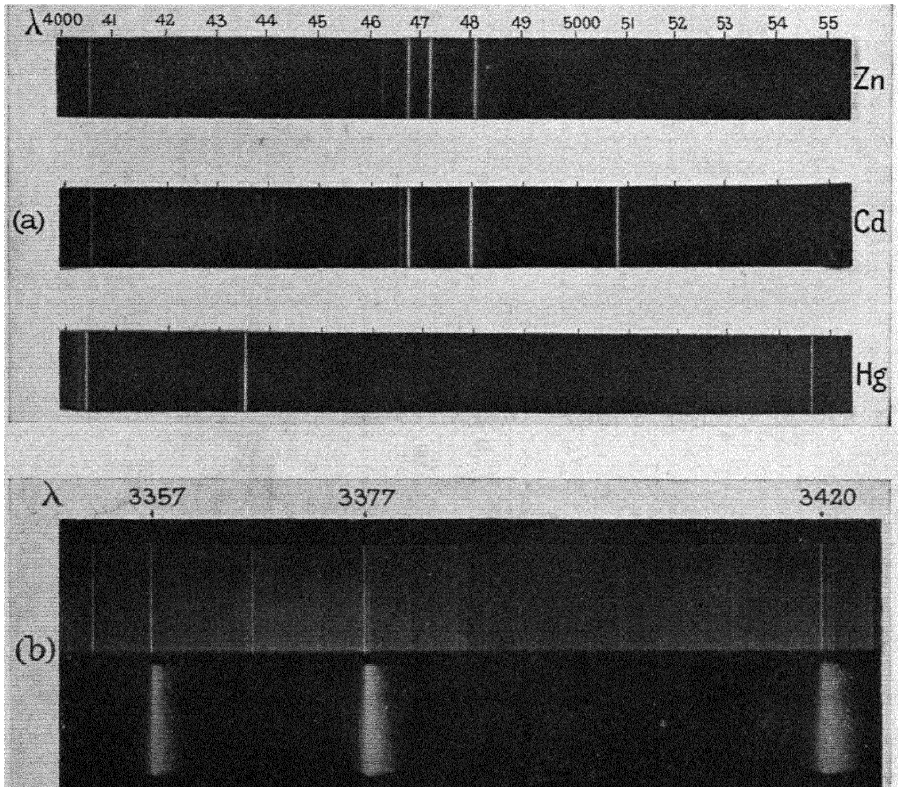


PLATE II.—ARC SPECTRA OF CADMIUM, ZINC AND MAGNESIUM, SHOWING SERIES TRIPLETS



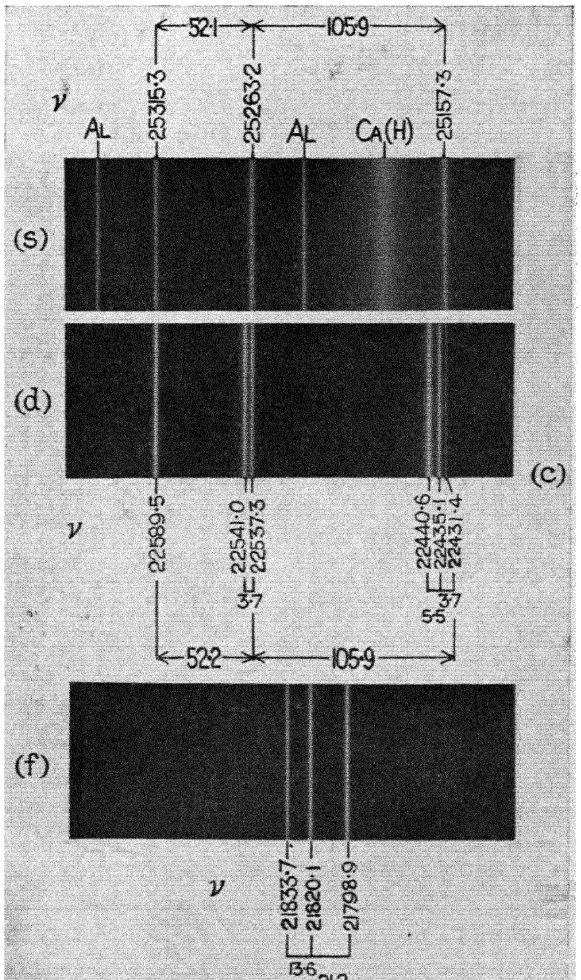
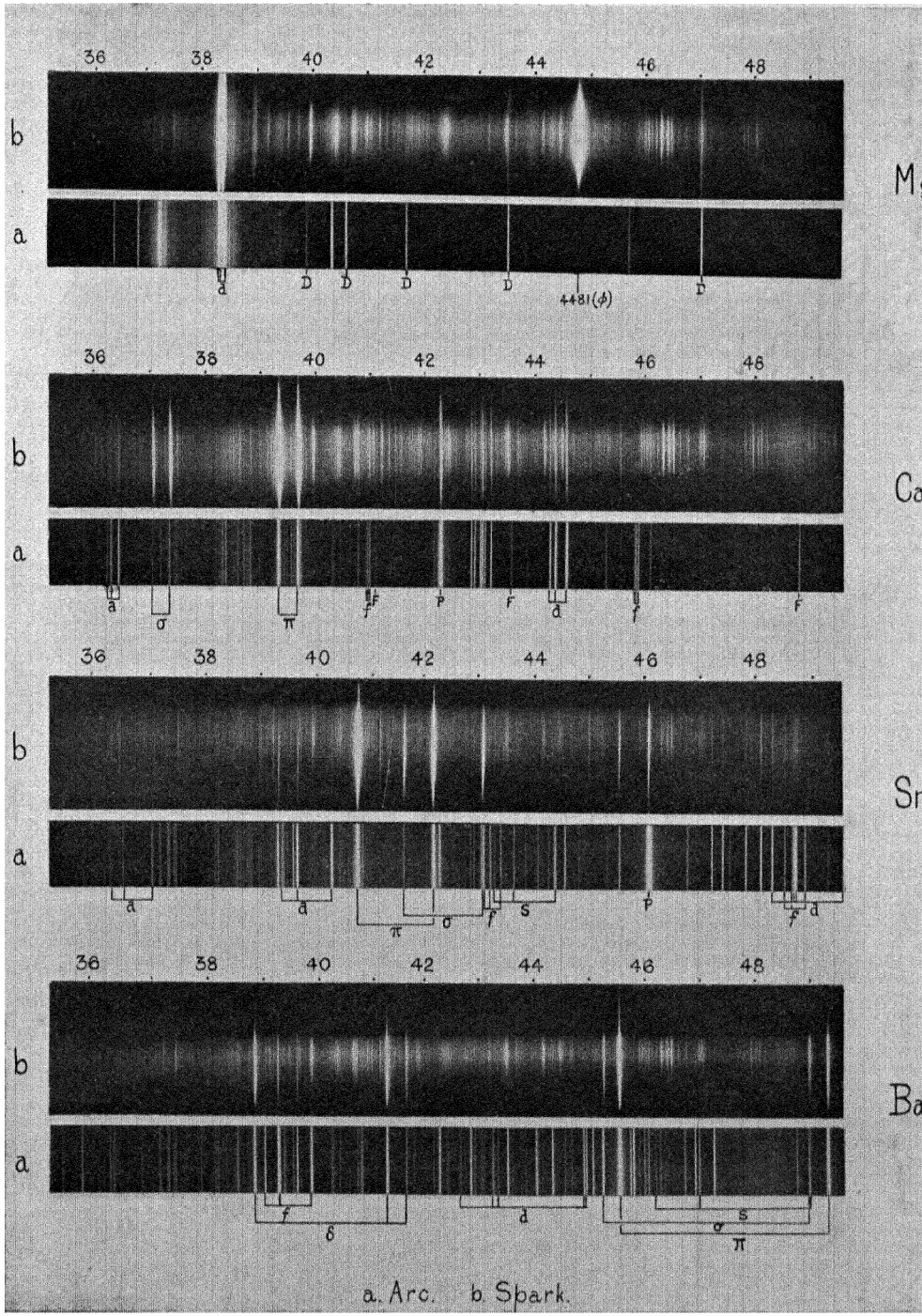


PLATE III

(*a*) RELATIVE SEPARATIONS OF TRIPLETS OF ZINC CADMIUM AND MERCURY
(*b*) SATELLITES IN FUNDAMENTAL TRIPLET OF BARIUM
(*c*) COMPARISON OF SHARP DIFFUSE AND FUNDAMENTAL TRIPLETS OF CALCIUM



a Arc b Spark

PLATE IV.—ARC AND SPARK SPECTRA OF MAGNESIUM, CALCIUM STRONTIUM AND BARIUM

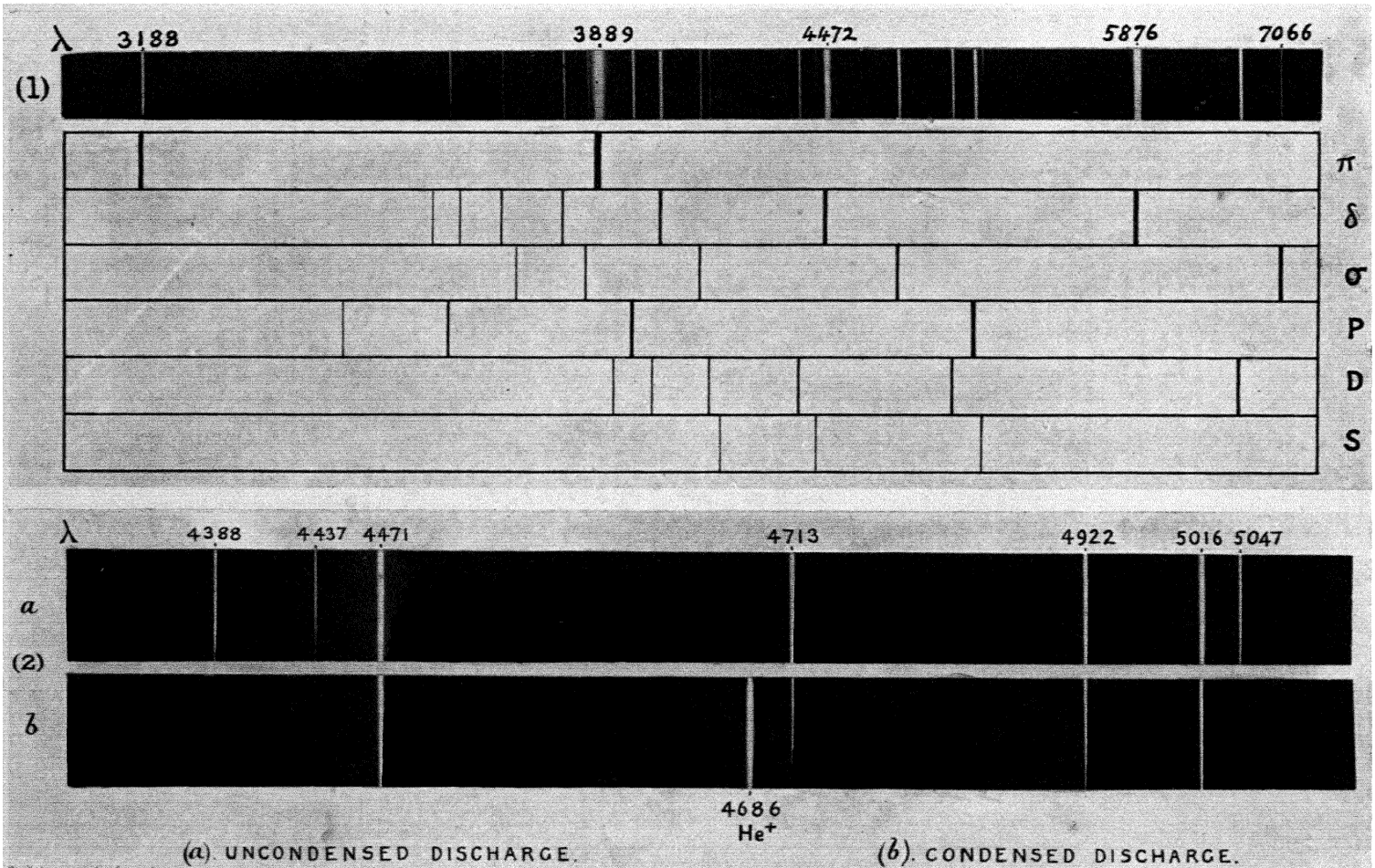


PLATE V.—SPECTRA OF HELIUM AND IONISED HELIUM