Bakerian Lecture: The Spectrum of Silicon at Successive Stages of Ionisation

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PHILOSOPHICAL TRANSACTIONS.

I. BAKERIAN LECTURE.—*The Spectrum of Silicon at Successive Stages of Ionisation.*

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[PLATES 1—3.]

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TABLES.

I. INTRODUCTORY.

The spectrum of silicon has been the subject of numerous investigations, of which a convenient summary to the year 1912 has been given by KAYSER.* The spectrum is of special interest on account of the remarkable series of variations which accompany changes in the experimental conditions. These changes were first systematically investigated by LOCKYER,† who further showed that the different groups of lines which were developed with increasing intensity of discharge appeared in the spectra of stars following each other in order of increasing temperature.‡ Four distinct groups of lines were recognised by LOCKYER, namely:—

Group I.   .. λλ 3905·8, 4103·2
Group II.   .. λλ 3853·9, 3856·1, 3862·7, 4128·1, 4131·1, 5042, 5057.
Group III. .. λλ 4552·8, 4568·0, 4574·9.
Group IV.   .. λλ 4089·1, 4116·4.§

The lines of Group I correspond to the arc spectrum, and are most strongly developed in stars approximating to the solar or G type. The chief lines of Group II are produced in the ordinary spark spectrum, but the fainter lines are best obtained in vacuum tubes; they have their greatest relative importance in stars of types F and A. Lines

* 'Handbuch der Spectroscopie,' vol. 6, p. 478.
† 'Roy. Soc. Proc.,' vol. 65, p. 449 (1899); vol. 67, p. 403 (1901); vol. 74, p. 296 (1904).
‡ See also "Catalogue of 470 of the Brighter Stars," 'Solar Physics Committee' (1902).
§ *Note.*—Another line at λ 4097, at first included in this group, was afterwards shown by LUNT to be due to an impurity, and was subsequently identified by LOCKYER, BAXANDALL, and BUTLER as an enhanced line of nitrogen. ('Roy. Soc. Proc.,' A, vol. 82, p. 532 (1909)).

of Groups III and IV are also most effectively observed in vacuum tubes, and are produced in turn as the energy of the discharge is increased; they occur in successively higher stages of the stellar sequence, those of Group IV not appearing until the hotter B stars are reached.

LOCKYER's grouping of the lines was confirmed by LUNT,* who made an extensive series of experiments, mainly on the chloride and fluoride of silicon. These observations, however, like those of LOCKYER, only extended over the comparatively small part of the spectrum which can be photographed in the stars with ordinary photographic plates.

A valuable investigation of the spectra of the chloride and fluoride of silicon was afterwards made by PORLEZZA,† covering the region λ 6371 to λ 3146. Several previously unrecorded lines were noted, especially in the region between λ 5200 and λ 5900, but no attempt was made to classify the lines in the different groups, and the wavelengths do not appear to be of a high order of accuracy.

An account of the spark spectrum of pure elementary silicon, over the range λ 6371 to λ 2124, was given by CROOKES‡ in 1914, and the spark spectrum in the region λ 2124 to λ 1842 was observed a little later by McLENNAN and EDWARDS.§

Many lines not recorded by previous observers were noted by SAWYER and PATON ‖ in the spectrum of a powerful " vacuum spark " discharge. These observations covered the region λ 6700 to λ 2100, but the resolution was not great and the wave-lengths were only considered to be correct within one or two-tenths of an angstrom. No attempt was made to classify the lines, but all the more important lines are included among those previously observed in the preparation of the present paper.¶

For completeness, it may be added that accurate determinations of the wave-lengths of nine silicon lines, which are of importance in connection with the observation of stellar radial velocities, have been made by H. BARRELL in connection with the present series of observations.**

A comparison of the various records shows considerable divergencies in the wave-lengths assigned to the same lines, and even the silicon origin of some of the lines has remained in doubt. There has also been no systematic study of the different groups of

* ' Roy. Soc. Proc.,' vol. 65, p. 448 (1899); vol. 66, p. 44 (1899); A, vol. 76, p. 118 (1905); ' Annals of the Cape Observatory,' vol. 10, Part II. (1905).

† ' Gaz. Chim. Ital.,' vol. 42, Part 2, p. 42 (1912).

‡ ' Roy. Soc. Proc.,' A, vol. 90, p. 572 (1914).

§ ' Phil. Mag.,' Ser. 6, vol. 30, p. 482 (1915).

‖ ' Astrophys. Jour.,' vol. 57, p. 279 (1923).

¶ Important observations in the extreme ultra-violet have been made by BOWEN and MILLIKAN (' Physical Review,' vol. 23, p. 1 (1924)) and by McLENNAN and SHAVER (' Trans. Roy. Soc. Canada,' vol. 18, p. 1 (1924)). These have confirmed the existence of several lines of the fourth spectrum of silicon previously predicted by the author's observations, as indicated in Table 13. McLENNAN and SHAVER have also observed the arc spectrum in the region λ 6320 to λ 11231.

** ' Monthly Notices, R.A.S.,' vol. 83, p. 322 (1923).

silicon lines over a wide range of spectrum such as is required in the investigation of spectral series. It, therefore, seemed desirable to make a more exhaustive investigation of the spectrum under different conditions, with a view to obtaining the wavelengths of the lines with greater precision and especially of obtaining the complete spectra represented by the different groups of LOCKYER. In this way it was hoped to obtain data which might lead to the identification of the series which characterise the different groups, and thence to a more complete physical explanation of the changes observed in the laboratory and in the stars.

The investigation has been in progress during several years, and suggestive results with regard to the series were early obtained.* Publication of details, however, was long delayed by the necessity of extending the observations into the Schumann region, in which it appeared that some of the more important lines for completely establishing the various series might be expected to occur. With the aid of a grant from the Government Grant Committee of the Royal Society a suitable instrument was obtained, after much unavoidable delay, and some of the desired observations were made.

The new observations revealed many lines in addition to those previously known, in all parts of the spectrum, and numerous series have been fully or partially established for the different groups of lines. In accordance with BOHR's theory, it results that the classification of silicon lines which was first deduced by LOCKYER, from the behaviour of the lines in the laboratory and stellar spectra, has a true physical basis, and that the successive groups represent successive stages of ionisation of the silicon atoms. This conclusion depends upon the evaluation of the series constant for the series lines of different groups.

On the nucleus theory of the atom, BOHR showed how the RYDBERG series constant could be derived theoretically for hydrogen, and indicated in a general way why the same constant should appear in the formulæ for other spectra. The theory also gave an entirely satisfactory explanation of the change from the ordinary to the enhanced spectrum in the case of helium, and in the Bakerian Lecture for 1914† it was shown by the present writer that a similar explanation was applicable to other elements. It appeared from these investigations that in passing from arc to spark lines, the series were of generally similar character, but that the series constant was changed from RYDBERG's R to 4 R.‡ In other words, the enhanced lines are produced by atoms which have lost an electron or have become ionised.

The theory further indicated the possible production of other series for which the constant would have the values 9 R, 16 R, and so on, if sufficient stimulus could be applied to remove additional electrons. The work of LOCKYER strongly suggested that examples of such new types of series might be found in a further study of the varying

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* A. FOWLER. "Report on Series in Line Spectra." 'Physical Society,' p. 164 (1922).

† 'Phil. Trans.,' A, vol. 214, p. 225 (1914).

‡ In former papers the series constant was indicated by N, but in agreement with certain other workers, R will be adopted for this constant in the present paper.

spectrum of silicon, as has proved to be the case. In the arc spectrum, the typical series appear to be very feebly developed, and the terms have not yet been fully determined, but the investigation has definitely proved that the series corresponding with the second, third and fourth silicon groups are characterised by the respective series constants 4 R, 9 R and 16 R. The four groups of LOCKYER are therefore to be interpreted as follows :—

Group   I.—Si   I, or Si $=$ neutral atoms.
Group   II.—Si II, or Si^+ $=$ singly-ionised atoms.
Group III.—Si III, or Si^{++} $=$ doubly-ionised atoms.
Group IV.—Si IV, or Si^{+++} $=$ trebly-ionised atoms.

The series systems consist alternately of triplets and doublets in accordance with the so-called spectroscopic " displacement law " of KOSSEL and SOMMERFELD.

While the present work has been in progress, a similar investigation of the successive spectra of aluminium, designated Al I, Al II, and Al III, has been made by PASCHEN.* Sodium, magnesium, aluminium and silicon have consecutive atomic numbers, and instructive comparisons may therefore be made of the spectra of Na I, Mg II, Al III and Si IV ; of Mg I, Al II and Si III ; and of Al I and Si II.

The chief results with regard to the series of Si IV have already been presented to the Society,† but some additional data have since become available. Detailed results relating to all the lines observed at the four stages of excitation are given in the present paper, and comparisons are made with the corresponding spectra of other elements which immediately precede silicon in the periodic table. A comprehensive catalogue of the lines observed at different stages is also included ; this may be expected to be of further use in connection with the observation of other spectra produced by strong discharges in vacuum tubes, since, under such conditions, silicon lines frequently appear in consequence of the decomposition of the glass.

II. OBSERVATIONAL DATA.

The Instruments Employed.

Numerous spectrographs were employed in the course of the investigation, some for preliminary observations over a large range, and others, of high dispersion, for the final determinations of wave-lengths. For measurements of the brighter lines in the visible region a 10-feet concave grating was used, chiefly in the first order, and the same instrument was used for selected regions in the ultra-violet, including λ 2218 to λ 2058. For most of the wave-length determinations in the ultra-violet as far as λ 2250, photographs were taken with a large quartz spectrograph of the Littrow type, constructed by Adam

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* ' Ann. d. Phys.,' vol. 71, p. 142 (1923) [Al III.] ; ' Ann. d. Phys.,' vol. 71, p. 537 (1923) [Al II.].
† ' Roy. Soc. Proc.,' A, vol. 103, p. 413 (1923).

Hilger, Ltd. The definition given by this instrument is extremely good, and the large scale does not involve unduly long exposures. The linear dispersion ranges from 12 A per mm. at λ 4000 to 4·5 A per mm. at λ 3000, and 2 A per mm. at λ 2300. A small quartz spectrograph by Bellingham and Stanley was used for the determination of the wave-lengths of lines between λ 2000 and λ 1841, the dispersion at λ 1900 being about 5·5 A per mm.*

The wave-lengths were interpolated in the usual manner with reference to standard lines of iron. So far as possible, the values for the standards were taken from the list adopted by the International Astronomical Union,† or from the well-known table by BURNS. Between λ 2374 and λ 2290 KAYSER's wave-lengths of iron lines, corrected to the International scale, were adopted as standards, and for the region beyond λ 2290, lines of aluminium and copper given by EDER.‡

Much labour has been expended in the effort to obtain wave-lengths of a high degree of accuracy. Those obtained with the grating are distinguished in the tables by being expressed to three decimal places, and are unlikely to be more than 0·01 A in error. The values determined with the large quartz spectrograph are probably less accurate, but the errors should not often exceed 0·02 A ; the large inclination of the photographic plate in this instrument, combined with want of perfect flatness of the plates, is probably responsible for the want of closer agreement in the values obtained from different photographs.

For the calculation of wave-numbers, the wave-lengths were corrected to vacuum by the tables published by the Washington Bureau of Standards.§

The Vacuum Spectrograph.

The vacuum spectrograph utilized for observations in the extreme ultra-violet was constructed by Adam Hilger, Ltd. It is provided with a 4-inch concave grating having a radius of 1 metre and 15,000 lines per inch. The grating was specially ruled at the Johns Hopkins University with a view to its use for the extreme ultra-violet, and has been found quite satisfactory for observations down to about λ 800. The wave-lengths from different plates, however, are less consistent than might have been expected, probably on account of irregularities in the sensitive films of the plates employed. The instrument has so far been mainly used with a fluorite window covering the slit, in order that vacuum tubes of silicon fluoride and sparks in hydrogen at atmospheric pressure might be used as sources. The region covered by the present observations has thus been mainly restricted to wave-lengths on the less refrangible side of λ 1250. The dispersion in the first order spectrum is 17·2 A per millimetre. Suitable standards

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* The author is indebted to the Government Grant Committee of the Royal Society for this instrument.

† 'Trans. Int. Ast. Union,' vol. 1, p. 41 (1922).

‡ 'Zeit. f. Wiss. Phot.,' vol. 14, p. 137 (1915).

§ 'Scientific Papers,' No. 327 (1918).

were provided by LYMAN's wave-lengths of aluminium lines, and by SIMEON's wave-lengths of carbon lines.* The adopted values for the silicon lines are probably correct within one- or two-tenths of an angstrom.

The author is indebted to Mr. F. SIMEON, of the research laboratory of Adam Hilger, Ltd., for placing at his disposal an excellent photograph of the silicon vacuum arc covering the region λ 1405–λ 990. This has provided a useful check on the author's observations in the common region, and some additional data in the region more refrangible than λ 1250. Some of the lines in this region have also been measured by BOWEN and MILLIKAN,† and the mean of SIMEON's and MILLIKAN's wave-lengths for one of the lines, 997·70, has been taken as a standard in the author's measurements, the other standard being the hydrogen line λ 1215·68.

The Arc Spectrum.

As a check on previous records of the arc spectrum by ROWLAND and others, photographs were taken of the spectrum of pure silica and of potassium fluosilicate when introduced into the carbon arc, and of the arc between pieces of fused silicon. With silica on poles of Acheson graphite the impurities were very slight, but with fused silicon lines of iron and other elements were sometimes numerous, especially in the ultra-violet. The lines which it is believed may certainly be attributed to silicon are those indicated as lines of Si I in Tables X and XII.

All the lines tabulated by ROWLAND‡ were observed, together with a few others, including some prominent lines in the ultra-violet which were outside the range of ROWLAND's observations.

It is of interest to note that three of the previously unrecorded arc lines of silicon have been found to correspond with three unidentified solar lines tabulated by ROWLAND, namely :—

Silicon Arc.		Sun.	
λ I. A.		λ ROWLAND.	Intensity.
5797·855		5798·077	3
5793·070		5793·292	3
5780·378		5780·600	0

Besides the lines of Group I, EXNER and HASCHEK have included the red pair of Group II (λλ 6371, 6347) as appearing faintly in the arc spectrum. As in the case of magnesium, and many other elements, however, these spark lines are restricted to a region very close to the poles of the arc. This method of producing the red pair was, in fact, employed by the author in 1906, in the identification of the red pair of lines in the solar and chromospheric spectra.§

* ' Roy. Soc. Proc.,' A, vol. 102, p. 484 (1922) ; vol. 104, p. 368 (1923).
† ' Physical Review,' vol. 23, p. 1 (1924).
‡ " New Table of Standard Wave-lengths," *Astronomy and Astrophysics*, vol. 12, p. 321 (1893).
§ ' Monthly Notices, R.A.S.,' vol. 67, p. 157 (1906).

In the far ultra-violet, the silicon arc also shows a number of well-marked flutings, which were first recorded by DE GRAMONT and DE WATTEVILLE.* These flutings have also been observed under other conditions, and it would appear that they have been correctly attributed to the oxide of silicon.†

The Spark Spectrum.

For observations of the spark spectrum the ordinary condensed discharge from a 12-inch induction coil was passed between poles of fused silicon.

All the brighter arc lines in the ultra-violet appear in this spectrum, as do also the brighter lines of Si II. Many of the fainter lines of Si II which appear in vacuum tubes, however, do not certainly occur in the spark, probably because under these conditions they are very diffuse as well as faint. Some of the brighter lines of Si III are also present, and even the brighter lines of Si IV may be found in the regions near the electrodes, as was also noted by LUNT and by LOCKYER, BAXANDALL and BUTLER. Photographs of the spark in an atmosphere of hydrogen, which were especially necessary in observations in the Schumann region, showed an increased development of lines belonging to Si III and Si IV; the comparison of sparks with and without self-induction was of great assistance in distinguishing lines of different classes.

The silicon lines attributed to Si II are collected in Tables X and XIII. It is to be understood that only the more prominent of these are observed in the ordinary spark spectrum, and that they are accompanied by the brighter lines of Si I and Si III.

The "spark" spectrum was further studied by observations of the arc between poles of fused silicon *in vacuo*. Under these conditions the chief lines of Si II were well developed, and occurred with perfect sharpness, so that wave-lengths could be determined with a high order of accuracy.

Two lines given by CROOKES as occurring in the spark spectrum at λ 3438·300 and λ 3247·551 (I.A.) have not been recorded by any other observer, and have not been confirmed; the second line is very close to the strong copper line 3247·53.

Several of the lines at first included by EXNER and HASCHEK as belonging to the silicon spark have already been shown to be due to impurities by EBERHARD and LUNT, namely, 4103·7, 4030·1, 4021·0, 3883·46 and 3853·62. In addition, lines given by EXNER and HASCHEK at 2446·63 and 2443·91 have not been observed.

The original table of spark lines given by EDER and VALENTA (as quoted in KAYSER's 'Spectroscopie,' vol. 6, p. 490) includes several faint lines which have also not been traced in the present series of observations; these are not in the list given by EDER and VALENTA in their well-known 'Atlas of Spectra,' and are probably due to impurities.

As a general remark, it may be noted that the spark does not provide so useful a

* 'Comptes Rendus,' vol. 147, p. 239 (1908).
† See also W. JEVONS: 'Roy. Soc. Proc.,' vol. 106, p. 174 (1924).

means of investigating the lines of Si II as is provided by observations of silicon compounds in vacuum tubes.

Vacuum Tube Spectra.

For observations of vacuum tube spectra the tubes were filled with the vapour of silicon chloride, or with silicon tetrafluoride, and subjected at various pressures to induction-coil discharges of varying intensity. In agreement with the observations previously made by LUNT,* it was found that lines of the higher silicon groups were more satisfactorily obtained from the tetrafluoride than from the chloride, and most of the observations were, therefore, made on the tetrafluoride.

The capillary tubes used were observed "end-on" through quartz windows, thus permitting photographs to be taken in the ultra violet. For the special development of lines of Si II it was found advantageous to use rather wide tubes, ranging up to 1·5 mm. internal diameter. For Si IV tubes of internal diameter 1 mm. or less gave the best results. For work with the vacuum spectrograph the discharge tube was provided with a fluorite window, which was sealed on the slit plate.

Silicon chloride obtained commercially was found to be of a high degree of purity, so that when care was taken to exclude atmospheric gases the only lines which could not be assigned to silicon or chlorine were a few lines due to carbon.

In the earlier experiments silicon tetrafluoride was prepared by the action of sulphuric acid on a mixture of calcium fluoride and silica. Later, on the suggestion of Prof. SMITHELLS, it was found more convenient to prepare the gas by heating barium fluosilicate. Before passing to the discharge tube the gas traversed a tube containing phosphorus pentoxide, in order to remove water vapour, and before reaching the pump it successively passed over potash and phosphorus pentoxide. The latter arrangement effectively prevented the gas entering the pump, provided that the exhaustion was not too rapid. To reduce inevitable carbon impurities, all stopcocks were lubricated as sparingly as possible with tap grease. It was found convenient to have a large bulb immediately following the hard glass generating tube, for the purpose of storing a quantity of the gas at nearly atmospheric pressure. Small quantities were then admitted to the discharge tube, as required, by the usual arrangement of a short length of tube between two taps. This small compartment was necessary for the readjustment of the pressure, especially during the passage of strong discharges. A barometer tube on the high-pressure side of the apparatus, which could be shut off at will by means of a stopcock, was useful as a safety valve and pressure indicator.

With ordinary precautions there was no difficulty in obtaining the gas with the requisite purity, except for carbon impurities, which appear to be almost unavoidable, and sometimes chlorine. The degree of purity and the character of the spectrum under the action of any particular discharge could usually be sufficiently judged by visual observations, but when using the vacuum spectrograph, photographs in the

* ' Roy. Soc. Proc.,' A, vol. 76, p. 118 (1905).

ultra-violet were also frequently taken through a second quartz window to indicate more surely the stage of ionisation which had been reached.

The uncondensed discharge through silicon tetrafluoride is of a deep blue colour, and the predominant feature is a group of bands in the region λ 4200 — λ 4500, due to the undissociated gas; bands are also numerous from about λ 3100 to λ 2300, and the brighter lines of Si I also appear. The bands do not appear in the capillary when condensed discharges are employed, but they often appear in the photographs of end-on tubes on account of the discharge in the wider portions. By appropriate adjustment of the condenser and air-gap, it was easy to obtain the equivalent of the ordinary spark spectrum, showing the lines of Si II at maximum intensity and much sharper than in the spark. Increased intensity of discharge gives a special development of lines of Si III; and, finally, by considerably reducing the pressure of the gas, the lines of Si IV may be obtained with maximum intensity. It should be observed, however, that lines of Si IV and Si III nearly always appear together. Examples of the photographs, with full descriptions, are given later.

Photographs were also taken of the spectra given by strong discharges through highly exhausted glass or quartz tubes, the tubes being originally filled with helium or oxygen. Under these conditions, the lines of Si IV were obtained with their greatest intensity. The silicon lines could be identified by their coincidences with the lines obtained in other ways, and by comparison with the spectrum of oxygen which was under investigation in the laboratory at the same time; the silicon lines were also distinguishable by their restriction to a comparatively small part of the width of the spectrum, while the oxygen lines extended completely across the spectrum. In these tubes many of the arc lines were suppressed, or nearly so, and lines of Group II considerably reduced in relative intensity. These observations provided the most trustworthy means of distinguishing the lines of silicon from those due to fluorine.

The same phenomena were observed with tubes of glass, but in that case it was observed, in accordance with the previous observations of LUNT, that lines of calcium, sodium and other elements were also obtained.

All the lines catalogued by LUNT and by PORLEZZA between the red and λ 3190 appear on the present series of photographs (with the exception of a faint line at 3191·15), together with many additional lines.

III. THEORETICAL PREDICTIONS AND NOMENCLATURE.

The Series Constant.

In order to avoid repetition, it will be convenient to refer next to the theoretical predictions as to the character of the spectra which may be expected to appear at successive stages of ionisation.

BOHR's theoretical formula for the series constant may be written

$$C = \frac{2\pi^2 e^2 m}{ch^3} \frac{M}{M + m} (ne)^2$$

where e and m respectively indicate the charge and mass of the electron, M the mass of the nucleus of the atom, c the velocity of light, h PLANCK's constant, and ne the net charge of the " core," or rest of the atom, with respect to the " series electron " which generates the spectrum by its quantum changes of orbit.

In the case of arc spectra, n has unit value and the series constant, apart from the term correcting for the mass of the nucleus, is equal to the hydrogen constant R. The factor $M/(M + m)$ differs very little from unity and has only a small influence on the series constant. The so-called spark spectrum is produced when the exciting agency is sufficiently powerful to remove one of the electrons out of the range of effective action of the nucleus. The atom is then ionised, and the spectrum is produced by one of the next outermost electrons. This interacts with the remainder of the atom, which now has a net positive charge $2e$, and the series constant becomes 4R. This predicted change, as previously mentioned, was verified by the author in the Bakerian Lecture of 1914. The theory further indicated that atoms which have lost two electrons, or have become doubly ionised, would be found to be characterised by series involving the constant 9 R, and so on. The theoretical prediction has now been verified in the case of silicon so far as trebly-ionised atoms, which have 16R for the series constant. The degree of ionisation is, in fact, most surely indicated by the value of the corresponding constant for the series.

Alternating Types of Series.

The theory further indicates that the spectra obtained at successive stages of ionisation should vary in type. The familiar arc series of sodium, magnesium and aluminium, together with the author's previous work on the spark spectrum of magnesium, and PASCHEN's work on ionised aluminium* provide material for a nearly complete comparison with the four spectra of silicon. The relations to be expected may be shown as follows :—

	Group I. Doublets.	Group II. Triplets.	Group III. Doublets.	Group IV. Triplets.
$n = 1$	Na I	Mg I	Al I	Si I
C = R	11 +, 10 —	12 +, 11 —	13 +, 12 —	14 +, 13 —
$n = 2$	Mg II	Al II	Si II	
C = 4R	12 +, 10 —	13 +, 11 —	14 +, 12 —	
n = 3	Al III	Si III		
C = 9R	13 +, 10 —	14 +, 11 —		
$n = 4$	Si IV			
C = 16R	14 +, 10 —			

* *Loc. cit.*

c 2

Under each symbol the number preceding the + sign represents the nuclear charge, and that preceding the − sign the number of external electrons apart from that which generates the spectrum, so that in the first row the atoms as a whole are neutral. The atomic numbers of Na, Mg, Al and Si are respectively 11, 12, 13, 14, and the neutral atoms give spectra consisting alternately of doublets and triplets.* The spectrum of neutral silicon (Si I) includes triplets and, as shown in the table, the spectrum of ionised silicon (Si II) may be expected to be similar to that of neutral aluminium (Al I) and to yield a system of doublets. In the same way, the spectra of Si III and Si IV were expected to resemble in type the spectra of Mg I and Na I respectively. All spectra in the same vertical column of the foregoing table should, in fact, be of the same type. Corresponding lines in the spectra, however, would be expected to be displaced to shorter wave-lengths as the degree of ionisation is increased, in consequence of the increased nuclear charge. These predictions have also been realised, as will presently appear.

Series Notation.

The series notation adopted in the present paper is mainly that of the author's " Report on Series," in which singlet terms are represented by mS, mP, mD, mF, doublets by $m\sigma$, $m\pi$, $m\delta$, $m\phi$, and triplets by ms, mp, md, and mf. In accordance with more recent usage, however, the multiple doublet and triplet terms have been modified as follows :—

	Doublets.			*Triplets.*	
Old	New		Old	New.	
δ'	δ_2		d'', d', d	d_3, d_2, d_1	
δ	δ_1		f'', f', f	f_3, f_2, f_1	

The nomenclature of the diffuse and fundamental terms is thus brought into accordance with that of the principal terms.

It is now recognized that there is no limit to the number of possible types of terms, and a nomenclature for types additional to the four earliest known has become necessary. The more familiar terms are characterized by azimuthal quantum numbers (k)† as follows :—

s, S or σ terms	$k = 1$
p, P or π ,,	$k = 2$
d, D, or δ ,,	$k = 3$
f, F, or ϕ ,,	$k = 4$

* Recent investigations of the more complex spectra of elements of the higher groups have shown that this sequence takes the form of alternate even and odd multiplicities. The maximum multiplicity increases by unity in successive groups, and is one greater than the number of the group in the periodic table. In Group I the maximum multiplicity is 2, in Group II it is 3, and the spectra are correspondingly simple. (See *e.g.*, A. LANDÉ, Zeit. f. Phys., vol. 15, p. 189 (1923).) This extended view of multiplicities, however, scarcely enters into the discussion of the spectra dealt with in the present communication, as the quintet terms expected in Si I appear to be absent or very feebly developed.

† Sommerfeld : ' Atomic Structure and Spectral Lines,' English edition, p. 365.

It is clear according to the general theory that there may be other types for which the characteristic azimuthal quantum numbers are higher than 4. In ordinary arc spectra, series involving such terms occur in the infra-red, and their true character has only been revealed through the occurrence of similar series in the ordinary region of observation in the spectra of ionised elements. Ionised magnesium, for example, includes a series which was approximately represented by $3\phi - m\phi$,[*] but the $m\phi$ terms were afterwards recognized by BOHR and others as a new set of terms, designated $m\phi'$, which differ but little from the $m\phi$ terms and approach still more closely to the terms of hydrogen.[†] In Al III and Si IV, this fifth set of terms combines with another set $m\phi''$ to produce a sixth type of series. The fifth and sixth series have been called by PASCHEN the Super-Bergmann ("Über-Bergmann") and Super-super-Bergmann ("Über-über-Bergmann") series respectively. Similar series in a triplet system would be designated f' and f''; ϕ' and f' are characterized by the azimuthal quantum number 5, and ϕ'', f'' by the number 6.

It would clearly have been inconvenient to adopt this notation permanently, and g has been substituted for f' by several workers. This modification has also been made in the present paper, and in view of the convenience of retaining the Greek letters for doublets the sixth series of terms will be indicated by k for triplet terms and κ for doublet terms. Thus :

Old Notation.	New Notation.	Az. Quant. No.
f', F', or ϕ'	g, G or γ	5
f'', F'', or ϕ''	k, K, or κ	6

The symbol used for a term will ordinarily give a sufficient indication of the associated azimuthal quantum number.

Numeration of Series Terms.

The values of the principal quantum numbers assigned to the various spectral terms by BOHR[‡] are very different from the numbers of RYDBERG or RITZ, and the ordinary series formulæ do not indicate them. On the new system groups of electrons in the normal atom, such as were previously considered to be arranged in rings about the nucleus, are assigned principal quantum numbers increasing outwards, the first (K) group having the quantum number 1, the second (L) group 2, and so on. The second ring or group is completed at neon (atomic number 10), and in the normal states of the atoms of elements having atomic numbers from 11 to 18 (argon) the outer electrons (M group) occupy orbits having the principal quantum number 3. The azimuthal quantum numbers associated with the normal states are indicated by the highest terms

[*] A. FOWLER : 'Phil. Trans.,' A, vol. 214, p. 253 (1914).
[†] 'Roy. Soc. Proc.,' A, vol. 103, p. 419 (1923).
[‡] 'Ann. d. Phys.,' vol. 71, p. 260 (1923).

of the spectral series in accordance with the previous remarks; for example, if the highest term be $2p$, a 2_2 orbit is indicated for the series electron. For circular orbits n and k are equal, and the greater the difference between n and k the greater will be the eccentricity of the orbit.

While BOHR's new system of numeration is of undoubted importance in theoretical discussions, it would seem to be more convenient to retain the older numbers for descriptive purposes. These have the advantage of being identical for corresponding lines in the spectra of different elements of the same group, and also of being directly related to the formulæ which are in general use for the approximate representation of series. Comparison with existing compilations of spectroscopic data will also be facilitated thereby.

In the present paper the RYDBERG-HICKS numeration will be adopted, as in the author's "Report on Series," but so far as possible an indication will be given of the alterations necessary for reduction to the BOHR system. In general, but not invariably, the number assigned to a term on the RYDBERG-HICKS system is the integral part of $\sqrt{R/\text{term}}$, *i.e.*, the integral part of the "effective quantum number."

The following comparison of the different systems of numeration as applied to the first terms of sodium, magnesium, and aluminium may be useful for reference.

	RYDBERG.			RITZ-PASCHEN.			BOHR.		
	Na	Mg	Al	Na	Mg	Al	Na	Mg	Al
Singlets . . . . . {		1 S			1 S			3 S	
		1 P			2 P			3 P	
		2 D			3 D			3 D	
		3 F			4 F			4 F	
Doublets . . . . . {	1 σ		2 σ*	1 s		2 s	3 s		4 s
	1 π		1 π	2 p		2 p	3 p		3 p
	2 δ		2 δ	3 d		3 d	3 d		3 d
	3 ϕ		3 ϕ	4 f		4 f	4 f		4 f
Triplets . . . . . {		2 s*			2 s			4 s	
		1 p			2 p			3 p	
		2 d			3 d			3 d	
		3 f			4 f			4 f	

* These are designated 1σ and $1s$ in the author's "Report on Series," but the original numeration of Rydberg is more appropriate, it being then supposed that the $1s$ term does not occur.

Inner Quantum Numbers.

In the consideration of some of the groups of lines which occur in the spectra of silicon, it becomes necessary to refer to the so-called "inner quantum numbers" (j) which

have been assigned to the various types of spectral terms by SOMMERFELD and LANDÉ.[*] For the purposes of the present paper it will suffice to note the following :—

	Singlets.				Doublets.					Triplets.						
Terms	S	P	D	F	σ	π_1	π_2	δ_1	δ_2	s	p_1	p_2	p_3	d_1	d_2	d_3
j	0	1	2	3	1	2	1	3	2	1	2	1	0	3	2	1

Ordinary terms combine with each other in accordance with the selection rule $\Delta j = \pm 1$ or 0, except that the transition 0 to 0 does not occur. Combinations are further subject to the selection rule for azimuthal quantum numbers, $\Delta k = \pm 1$.

There is another class of terms, usually designated p', d', etc., which do not form part of the regular sequences, and are possibly due to the simultaneous transitions of two electrons with the emission of a single quantum of energy.[†] These are subject to the selection rule for inner quantum numbers, but the ordinary azimuthal quantum condition for their combination with the regular terms appears to be replaced by $\Delta k = 0$.[‡]

IV. REGULARITIES IN THE SPECTRUM OF Si I.

General Features of the Spectrum.

In the region extending from the red about $\lambda\,6700$ to the ultra-violet at $\lambda\,2000$ the arc spectrum of silicon includes 45 lines, of which only 13 occur in the visible spectrum, and only four in the region between $\lambda\,3900$ and $\lambda\,2640$. Several of the lines in the ultra-violet are of great intensity, but in the visible spectrum the lines are relatively weak. Several of the ultra-violet lines are easily reversed in the arc.

A comparison of the arc and spark spectra shows that enhanced lines do not appear at all in the arc, except in the region close to the poles when elementary silicon is employed, and all the lines which appear in the middle of an ordinary arc have accordingly been assigned to Si I. The wave-lengths, intensities, and wave-numbers of the lines between $\lambda\,6700$ and $\lambda\,2000$ are collected in Table X and of those between $\lambda\,2000$ and $\lambda\,1840$ in Table XII.

The complete series arrangement of the lines of Si I has not yet been traced, but it seems sufficiently clear that the main features arise from triplet and singlet terms. The triplet series, however, are but feebly represented, and as the first members occur far in the ultra-violet, succeeding members would only be expected as weak lines in the early Schumann region.

* ' Zeit. f. Phys.,' vol. 15, p. 189 (1923).
† See ' Roy. Soc. Proc.,' A, vol. 107, p. 39 (1925).
‡ LAPORTE : ' Zeit. f. Phys.,' vol. 26, p. 16 (1924).

Triplets of Si I.

A triplet of the sharp series and another of the diffuse series are unmistakable, namely :—

	Sharp Triplet.			Diffuse Triplet.		
λ, Int.	ν	$\Delta\nu$		λ, Int.	ν	$\Delta\nu$
2452·136 (3)	40768·42			2218·917 (1)	45052·96	
		146·12				17·00
2443·378 (3)	40914·54			2218·080 (2)	45069·96	
		77·10				28·36
2438·782 (3)	40991·64			2216·165 (4)	45098·32	
						146·03
				2211·750 (2)	45198·92	
						17·15
				2210·912 (3)	45216·07	
						77·17
				2207·980 (2)	45276·09	

A careful search has been made for other triplets, but with no certain results. There are, however, three lines with apparently the same separations forming part of an isolated group of five lines beginning at λ 1881·6.* Details of these lines are as follows :—

λ, Int.	ν	$\Delta\nu$
1880·71 (1)	53171	
		147
1875·54 (2)	53318	
		76
1872·87 (2)	53394	

The first line, however, which would be expected to be the strongest in a regular series, is definitely the weakest of the three, and the agreement in separations is possibly accidental. If regarded as the second $p\,s$ triplet, the value of p given by a RYDBERG formula would be about 64100.

Apart from this, there are no direct means for the determination of even the approximate limits of the triplet series.† There are also no arc lines in the less refrangible part of the spectrum which seem at all likely to represent an associated

* The possibility of these lines forming a triplet was first suggested to the author by Prof. McLENNAN.

† *Note.*—When the lecture was delivered, a limit of 85000 was considered to be a probable value for the triplet series, on the ground that in most of the known series of triplets the limit is rather more than double the wave-number of the first sharp triplet. It has since been noticed, however, that in most series the ratio of the limit to the first sharp triplet tends to diminish as the wave-number of the triplet increases, and the estimate was probably too high.

" principal " series $(2s - mp)$, and no suitable representatives of a fundamental series $(2d - mf)$, having separations $\Delta d_{21} = 28$ and $\Delta d_{32} = 17$. In view of the feeble development of the triplets themselves, it would seem that these series do not occur with sufficient intensity to appear in the present records of the spectrum.

Multiplets of Si I.

Some of the most intense lines of the arc spectrum are included in the well-known characteristic group of six lines extending from $\lambda\,2506$ to $\lambda\,2528$, all of which are reversed in the arc. These form a pp' multiplet, involving the triplet separations noted above, and it follows that the first terms of the combinations which give rise to the lines must be $1p_1$, $1p_2$ and $1p_3$. The group may be represented schematically as below, where numbers in brackets following the wave-numbers represent intensities and the inner quantum numbers (j) are indicated by numbers beneath or alongside the term symbols :

p_1		p_2		p_3		j
(2)		(1)		(0)		
		39605·89 (8)			p'_3	(0)
		77·14				
39537·01 (9)	*146·02*	39683·03 (7)	*77·01*	39760·04 (7)	p'_2	(1)
194·72		*194·80*				
39731·73 (10)	*146·10*	39877·83 (9)			p'_1	(2)

A prominent group of lines beginning with $\lambda\,1988$ also consists of six strong lines and may be represented in a similar manner ; namely

p_1		p_2		p_3		j
(2)		(1)		(0)		
50277·3 (4R)	*146·3*	50423·6 (3)			p''_1	(2)
66·8		*67·2*				
50344·1 (2)	*146·7*	50490·8 (2)	*77·1*	50567·9 (3)	p''_2	(1)
		35·9				
		50526·7 (2)			p''_3	(0)

The wave-numbers in this group are subject to a little uncertainty, mainly for lack of good standards of reference, but it is evident that the combinations involve the regular p terms and another set of terms of similar type represented by p''. It will be observed that the latter terms are in reverse order in this multiplet, the largest term being p''_1.

All the terms entering into the above multiplets clearly belong to triplet systems. No multiplets involving quintet terms, such as might have been expected from the sequence of multiplicities to which reference has previously been made have yet been identified.

It may be further remarked that, although the actual values of the various p terms cannot yet be stated, their differences are known with considerable accuracy. In particular, it will be useful to note the difference $1p'_2 - 1s$:

$$\left.\begin{array}{l} 1p_1 - 1s \ \ = \ 40768 \cdot 42 \\ 1p_1 - 1p'_2 = \ 39537 \cdot 01 \end{array}\right\} 1p'_2 - 1s \ = \ 1231 \cdot 41$$

$$\left.\begin{array}{l} 1p_2 - 1s \ \ = \ 40914 \cdot 54 \\ 1p_2 - 1p'_2 = \ 39683 \cdot 03 \end{array}\right\} 1p'_2 - 1s \ = \ 1231 \cdot 51$$

$$\left.\begin{array}{l} 1p_3 - 1s \ \ = \ 40991 \cdot 64 \\ 1p_3 - 1p'_2 = \ 39760 \cdot 04 \end{array}\right\} 1p'_2 - 1s \ = \ 1231 \cdot 60$$

$$\text{Mean, } 1p'_2 - 1s \ = \ \underline{1231 \cdot 51}$$

The Singlet Series of Si I.

Six of the stronger singlets, all of which can be obtained as reversed lines in the arc, can be arranged in two series, which are apparently to be identified as the sharp and diffuse series. A fourth line of the sharp series is suggested by the greater intensity of the more refrangible component of a pair of Si II lines, $\lambda\lambda$ 1817, 1808, in a photograph of the silicon spark in hydrogen with large self-induction. This is near the expected position of the next member of the sharp series and has been regarded as such.

The data and formula for the sharp series, as calculated from the last three lines, are as follows :—

λ, Int.	ν		
2881 ·585 (10R)	34692 ·97		
2124 ·140 (6R)	47062 ·94	$1P = 60072$	
1901 ·00 (5R)	52603 ·9		$mS = R\Big/\!\left(m + 0 \cdot 689685 + \dfrac{0 \cdot 427838}{m}\right)^2.$
1808 ·14	55305		

The correcting term is unusually large, but, notwithstanding this, the extrapolated wave-number for the first line only differs by 919 from the observed value. If calculated from the first three lines, $1p = 60020$.

The data and formula for the diffuse series are :—

λ, Int.	ν	
2435·159 (8R)	41052·61	
2058·20 (5R)	48570·51	
1893·02 (2R)	52832	

$$1P = 59339\cdot0$$
$$mD = R\bigg/\left(m + 0\cdot933784 + \frac{0\cdot515257}{m}\right)^2.$$

The correcting term is again exceptionally large, so that neither of the series closely follows a RYDBERG formula. The two values for 1P also differ more than usual, but as the sharp series is generally more accurately represented than the diffuse, the value from the sharp series has been adopted ; namely, 1P = 60072.

With this limit, the terms and effective quantum numbers are :—

Terms.	$\sqrt{R/\text{Term.}}$	Terms.	$\sqrt{R/\text{Term.}}$
1S = 25379·03	2·078837	1D = 19019·39	2·401387
2S = 13009·06	2·903604	2D = 11502·49	3·087909
3S = 7468·1	3·832263	3D = 7240·2	3·892110
4S = 4767	4·796648		

The increase in the successive effective quantum numbers departs much more from unity than in most of the known series, but the fact that all the lines are readily reversed in the arc is strongly in favour of the above arrangement, in which the largest term is 1P.

Other Regularities in Si I.

A remarkable feature of the silicon arc spectrum is the occurrence of the separation $1p'_2 - 1s$ in connection with some of the strong singlets, including the line which has been designated 1P — 1S. Thus :—

$$\left.\begin{array}{l} 25597\cdot61 \ (9) - 24365\cdot89 \ (5) = 1231\cdot72 \\ 34692\cdot97 \ (10) - 33461\cdot39 \ (5) = 1231\cdot58 \end{array}\right\} = 1p'_2 - 1s.$$

These separations may be considered to be equal within the limits of observational errors, and their significance seems to be assured by the fact that the lines in question are strong and well separated from neighbouring lines. Further combinations between triplet and singlet terms are suggested by the following lines :—

ν	ν	$\Delta\nu$	
17645·64 (1) —	17568·52 (2) =	77·12	$= 1p'_3 - 1p'_2 = 1p_3 - 1p_2$
17707·97 (2) —	17513·19 (5) =	194·78	$= 1p'_2 - 1p'_1$
33656·27 (1) —	33461·39 (5) =	194·88	$= 1p'_2 - 1p'_1$

The line 33461, it should be noted, has already been included in the above consideration of the separation $1p'_2 - 1s$.

Much time has been expended in attempting to trace the connection between the triplet and singlet systems, but no satisfactory conclusions have yet been reached. There are sufficient indications, however, that the highest term will be found to be a P or a p term, and since the principal quantum number must be 3, it is probable that the series electron normally occupies a 3_2 orbit.

As the term $1p$ has not yet been determined, the first ionisation potential of silicon cannot be stated. The value of the term 1P, however, indicates that the ionisation potential cannot be less than 7·5 volts.

V. THE DOUBLET SERIES OF SI II (SI⁺).

General Remarks.

The spectrum of Si II forms a doublet system, some of the leading members of which have long been familiar from their occurrence in the ordinary spark spectrum.

From the beginning of the research it seemed sufficiently obvious by inspection that the red pair at $\lambda\lambda$ 6371, 6347, the yellow pair at $\lambda\lambda$ 5979, 5958, and the green pair at $\lambda\lambda$ 5056, 5041, were respectively the first members of principal, sharp and diffuse series, having a wave-number separation approximating to 60. Other members of the series, however, long eluded detection, and it now appears that the difficulty was due to the very rapid fall of intensity in passing along the respective series. This is especially the case in the principal series, where even the second member is very faint notwithstanding the great brightness of the pair in the red. One additional pair was found in the observations of silicon chloride, but the most complete representation of the doublets was obtained in the experiments on silicon tetrafluoride. In the latter case the lines appear as well-isolated pairs with appropriate separation, and there can be no doubt as to their association with the red, yellow, and green pairs. It is easily shown from the numerical data that the ordinary series constant is not applicable to these lines, and that a number of the order of 4R is required. The hydrogen value of 4R ($= 438713 \cdot 2$) has accordingly been adopted in the calculation of formulæ for these series.

The series $1\pi_{12} - m\sigma$ and $2\pi_{12} - m\sigma$ have been distinguished as the "first sharp" and "second sharp" series respectively; and similarly for the diffuse series. As in Al I, there is no 1σ term in Si II.

The lines which have been identified as belonging to Si II are collected in order of wave-length in Tables X and XIII.

The experimental behaviour of the classified lines included in the table accords with their assignment to Si II. There are also many lines which would seem to belong to Si II, on experimental grounds, for which no series relations have been found. Many such lines occur in the visible part of the spectrum, and the lines $\lambda\lambda$ 4188, 4191 first

observed by Lunt are noteworthy examples. In this connection it should be remembered that the spark spectrum includes lines which certainly belong to Si III, so that the occurrence of a line in the spark and not in the arc is not in itself a sure criterion for its classification as Si II. It is here that the vacuum tube spectra have the advantage, for spectra can be produced in which lines of Si II occur with great intensity, while lines of Si III are faint or absent.

The Series System of Si II.

The consistency of the allocations of the lines composing the Si II system of series is clearly shown by calculating formulæ for the separate series.

The Principal Series.—Three pairs of lines are available for the calculation of the limit of the principal series. The wave-numbers of the stronger components of the pairs and the formula derived from them are as follows :—

$$\left.\begin{aligned} 2\sigma - 2\pi_1 &= 15750\cdot90 \\ 2\sigma - 3\pi_1 &= 38384\cdot52 \\ 2\sigma - 4\pi_1 &= 48562\cdot70 \end{aligned}\right\} \quad \nu = 66297\cdot06 - 4R/(m + 1\cdot001375 - 0\cdot110567/m)^2.$$

The term $2\pi_1$ thus calculated is $50546\cdot16$ and it follows from the separation $\Delta\nu = 60$ that $2\pi_2 = 50606\cdot16$. These are in very satisfactory agreement with the values derived independently from the second sharp and diffuse series as indicated below.

The Second Sharp and Diffuse Series.—The sharp and diffuse series should give the same limits, apart from errors of observation and inadequacy of the type of formula employed, and these should agree with the values of 2π calculated from the principal series. The Hicks formulæ for the two series, and the data from which they were calculated, are as follows :—

$$\left.\begin{aligned} 2\pi_2 - 3\sigma &= 16780\cdot61 \\ 2\pi_2 - 4\sigma &= 29992\cdot96 \\ 2\pi_2 - 5\sigma &= 36772\cdot91 \end{aligned}\right\} \quad \nu = 50621\cdot40 - 4R/(m + 0\cdot644962 - 0\cdot133206/m)^2.$$

$$\left.\begin{aligned} 2\pi_2 - 3\delta_2 &= 19831\cdot58 \\ 2\pi_2 - 4\delta_2 &= 31203\cdot07 \\ 2\pi_2 - 5\delta_2 &= 37330\cdot50 \end{aligned}\right\} \quad \nu = 50710\cdot77 - 4R/(m + 0\cdot661311 + 0\cdot323876/m)^2.$$

The limits given by the Ritz formula in the form

$$\nu = A - 4R/[m + \mu + \alpha(A - \nu)]^2$$

lead to the values $50638\cdot13$ and $50683\cdot24$ respectively. All are as nearly in agreement with each other, and with the value $50606\cdot16$ calculated for $2\pi_2$ above, as is to be expected.

The Fundamental Series.—This is a series of narrow doublets, $\Delta\nu = 16\cdot6$, having a separation equal to that of the chief line and satellite in the first member of the diffuse series. The wave-numbers of the more refrangible components and the formula calculated from them are as follows :—

$$2\delta_2 - 3\phi = 24217\cdot69$$
$$2\delta_2 - 4\phi = 34421\cdot75$$
$$2\delta_2 - 5\phi = 39972\cdot60$$

$$\nu = 52483\cdot11 - 4R/(m + 0\cdot894930 + 0\cdot134295/m)^2,$$

i.e., $2\delta_2 = 52483\cdot11$; $2\delta_1 = 52466\cdot51$; $3\phi = 28265\cdot42$.

These values cannot be directly compared with the terms for the other series, as the first member of the diffuse series lies in the far infra-red and has not been observed. The value of the term 3ϕ, however, may be applied in connection with certain combination series to adjust all the limits, besides leading to values for 1π.

Combination Series.—Besides the series lines so far considered, there is a well-known group of three spark lines, beginning with λ 3862, which presents the appearance of an inverted diffuse set and must therefore have negative wave-numbers assigned to it. These cannot be deduced from any of the already known terms, but may be represented by introducing new terms of diffuse type, x_1 and x_2, as shown below.

The terms x, the magnitudes of which are indicated by the previously calculated values of 2π, combine with the ϕ terms to give a strong series of fundamental type in the extreme ultra-violet, beginning with a pair at λ 2073. For greater consistency of numerical results the wave-numbers for this pair have been slightly adjusted so as to make their separation $15\cdot91$, like that of the two more accurately measured lines $\nu\nu$ 25942, 25926, to which they are related. The observed wave-numbers $48232\cdot89$ and $48248\cdot49$ have thus been altered to $48232\cdot74$ and $48248\cdot65$. The terms x_1 and x_2 may then be calculated as follows :—

$$x_1 - 3\phi = 48232\cdot74 \qquad\qquad x_2 - 3\phi = 48248\cdot65$$
$$3\phi = 28265\cdot42 \qquad\qquad\qquad 3\phi = 28265\cdot42$$
$$x_1 = 76498\cdot16 \qquad\qquad\qquad x_2 = 76514\cdot07$$

For the calculation of $2\pi_1$ and $2\pi_2$ we have

$$2\pi_1 - x_2 = -25942\cdot05$$
$$2\pi_1 - x_1 = -25926\cdot14$$
$$2\pi_2 - x_2 = -25882\cdot04$$

$$2\pi_1 = 50572\cdot02$$
$$2\pi_2 = 50632\cdot03$$

The values of 2π thus obtained are very close to those calculated from the principal series and to the mean of those determined from the sharp series by the Hicks and Ritz

formulæ. These values will accordingly be adopted to fix the common limits of the second sharp and diffuse series ; at the same time the values above given for x_1 and x_2 are brought into accurate relationship with the other terms.

The term 2σ can at once be derived ; namely,

$$2\sigma - 2\pi_1 = 15750 \cdot 90$$

$$2\pi_1 = 50572 \cdot 02$$

$$2\sigma = 66322 \cdot 92$$

The First Sharp and Diffuse Series.—From general considerations, the chief lines of the Si II spectrum are to be expected in the extreme ultra-violet. In the photographs of this region there are two very striking pairs of lines, which are brought out by a moderate stimulus in silicon tetrafluoride, and which also appear in the silicon spark in hydrogen. One of these pairs, about $\lambda\,1533$, has been found to be the first member of the sharp series, while the other at $\lambda\lambda\,1817 \cdot 06,\ 1808 \cdot 14$, is a combination pair involving the x terms. A third pair, at $\lambda\lambda\,1265,\ 1260$, which also appears strongly in the photograph taken by SIMEON, is the first member of the diffuse series. Still another pair, about the lower wave-length of SIMEON's photograph, $\lambda\lambda\,993 \cdot 1,\ 990 \cdot 3$, is the second member of the first diffuse series. The common limits of the two series have been calculated from the sharp pair, $1\pi - 2\sigma$ with the aid of the previously determined term 2σ ; thus,

$$
\left.
\begin{aligned}
1\pi_1 - 2\sigma &= 65208 \\
1\pi_2 - 2\sigma &= 65495
\end{aligned}
\right\}
\qquad
\begin{aligned}
1\pi_1 &= 131531 \\
1\pi_2 &= 131818
\end{aligned}
$$

In this way all the limits required for the construction of the series table have been brought into proper relation with each other. Their general accuracy as regards the extreme ultra-violet is shown by the close agreement of the observed and calculated values for lines which have not been used in the determination of the limits.

The results of the discussion of the series of Si II are collected in Table I, which calls for little further explanation. The limits have been adopted from the calculations already given and the terms have been derived in the usual manner by subtracting the wave-numbers of observed lines from the corresponding limits. The numbers under m are those of the RYDBERG system, and the numbers $(+2)$, etc., indicate the alterations to give the numbers on BOHR's new system.

TABLE I.—Series of Si II (Si$^+$).

1st Sharp Series.—$1\pi - m\sigma$; $1\pi_1 = 131531$; $1\pi_2 = 131818$.

λ, Intensity.	ν	Δν.	m (+ 2).	mσ.
*1533·55 (10)	65208	287	(2)	66323
*1526·83 (8)	65495			
(1023·75)	(97680)	(287)	(3)	33851
(1020·75)	(97967)			
(901·78)	(110892)	(287)	(4)	20639
(899·45)	(111179)			

Principal Series.—$2\sigma - m\pi$; $2\sigma = 66322\cdot92$.

λ, Intensity.	ν.	Δν.	m (+ 2)	$m\pi_1$, $m\pi_2$
—1533·55 (10)	—65208	287	(1)	131531
—1526·83 (8)	—65495			131818
6347·091 (10)	15750·90	60·00	(2)	50572·02
6371·359 (8)	15690·90			50632·02
2604·44 (2)	38384·52	24·31	(3)	27938·40
2606·09 (1)	38360·21			27962·71
2058·53 (1)	48562·70	9·09	(4)	17760·2
2058·92 (0)	48553·61			17769·3

2nd Sharp Series.—$2\pi - m\sigma$; $2\pi_1 = 50572\cdot02$; $2\pi_2 = 50632\cdot02$.

λ, Intensity.	ν.	Δν.	m (+ 2)	mσ
—6347·091 (10)	—15750·90	60·00	(2)	66322·92
—6371·359 (8)	—15690·90			
5978·970 (5)	16720·63	59·98	(3)	33851·40
5957·612 (4)	16780·61			
3339·84 (3)	29932·98	59·98	(4)	20639·05
3333·16 (2)	29992·96			
2726·74 (2)	36662·99	59·92	(5)	13909·07
2722·29 (1)	36722·91			

* Used for calculation of $1\pi_1$, $1\pi_2$. A line of Si IV is apparently coincident with λ 1533·5.

TABLE I (continued).

1st Diffuse Series.—$1\pi - m\delta$; $1\pi_1 = 131531$; $1\pi_2 = 131818$.

Observed.		Calculated.		$\Delta\nu$.	$m(+1)$.	$m\delta_2, m\delta_1$.
λ vac., Intensity.	ν.	λ vac.	ν.			
*1265·04 (10)	79049	$\begin{cases}1265·06\\1264·78\end{cases}$	$\left.\begin{matrix}79048\\79065\end{matrix}\right\}$	16·6		52483
1260·66 (8)	79324	1260·48	79335	287	(2)	52466
*†993·09 (1)	100696	992·74	100731	287	(3)	30800
†990·32 (1)	100977	989·92	101018			

2nd Diffuse Series.—$2\pi - m\delta$; $2\pi_1 = 50572·02$; $2\pi_2 = 50632·02$.

λ, Intensity.	ν.	$\Delta\nu$.	$m(+1)$.	$m\delta_2, m\delta_1$.
Out of range	(−1911·09) (−1894·49) (−1851·09)	(16·60) (60·00)	(2)	52483·11 52466·51
5056·353 (2) 5055·975 (7) 5041·020 (5)	19771·60 19772·90 19831·58	1·30 59·98	(3)	30800·42 30799·12
*3210·04 (3) 3203·89 (2)	31143·30 31203·07	59·77	(4)	19428·8
*2682·27 (2) 2677·98 (1)	37270·80 37330·50	59·70	(5)	13301·4

Fundamental Series.—$2\delta - m\phi$; $2\delta_1 = 52466·51$; $2\delta_2 = 52483·11$.

λ, Intensity.	ν.	$\Delta\nu$.	$m(+1)$.	$m\phi$.
4130·884 (10) 4128·053 (8)	24201·08 24217·69	16·61	(3)	28265·42
2905·70 (3) 2904·29 (2)	34405·06 34421·75	16·69	(4)	18061·40
2501·99 (1) 2500·96 (1)	39956·15 39972·60	16·45	(5)	12510·43

* Satellites not resolved.
† From Simeon's photograph.

TABLE I (continued).

Combination Series of Si II.—$x - m\phi$; $x_1 = 76498 \cdot 16$; $x_2 = 76514 \cdot 07$.

λ, Intensity.	ν.	$\Delta\nu$.	Calculated.
—3853·657 (3) —3856·021 (8) —3862·592 (6)	—25942·05 —25926·14 —25882·04	15·91* 60·01	$\left.\begin{array}{l}2\pi_1 - x_2 \\ 2\pi_1 - x_1 \\ 2\pi_2 - x_2\end{array}\right\}$ Used for calculation of $2\pi_1,\ 2\pi_2.$
2072·61 (10) 2071·94 (8)	48232·89 48248·49	15·60	$\left.\begin{array}{l}x_1 - 3\phi \\ x_2 - 3\phi\end{array}\right\}$ Used for calculation of $x_1,\ x_2.$
(λ vac.) 1817·06 (10) 1808·14 (8)	 55034 55305	271	$\left\{\begin{array}{l}1\pi_1 - x_2 = 55017 = \lambda\,1817\cdot62 \\ 1\pi_1 - x_1 = 55033 = \lambda\,1817\cdot09 \\ 1\pi_2 - x_2 = 55304 = \lambda\,1808\cdot19\end{array}\right.$
1711·0 (6d ?)	58445		$\left\{\begin{array}{l}x_1 - 4\phi = 58437 = \lambda\,1711\cdot2 \\ x_2 - 4\phi = 58453 = \lambda\,1710\cdot8\end{array}\right.$
1563·1 (3d ?)	63975		$\left\{\begin{array}{l}x_1 - 5\phi = 63988 = \lambda\,1562\cdot8 \\ x_2 - 5\phi = 64004 = \lambda\,1562\cdot4\end{array}\right.$
1485·4 (3)	67322		$\left\{\begin{array}{l}x_1 - 6\phi\dagger = 67329 = \lambda\,1485\cdot2 \\ x_2 - 6\phi = 67345 = \lambda\,1484\cdot9\end{array}\right.$
1438·9 (1n)	69498		$\left\{\begin{array}{l}x_1 - 7\phi = 69494 = \lambda\,1439\cdot0 \\ x_2 - 7\phi = 69510 = \lambda\,1438\cdot6\end{array}\right.$
1408·8 (0n)	70982		$\left\{\begin{array}{l}x_1 - 8\phi = 70974 = \lambda\,1409\cdot0 \\ x_2 - 8\phi = 70990 = \lambda\,1408\cdot6\end{array}\right.$

* This is definitely smaller than the separation in the fundamental series (16·61).
† The formula gives $6\phi = 9169$, $7\phi = 7004$, $8\phi = 5524$.

In addition to the series shown in Table I, the " super-fundamental " series, $3\phi - m\gamma$, is possibly represented, but is somewhat doubtful, because of the absence of the first-expected member of the series. The possible second and third members are $\lambda\lambda 5202 \cdot 51$, $4683 \cdot 018$ ($\nu\nu$ 19216 ·15, 21347 ·79).   Taking these as $3\phi - 6\gamma$ and $3\phi - 7\gamma$ respectively, with $3\phi = 28265 \cdot 42$, the resulting terms are $6\gamma = 9049 \cdot 27$ and $7\gamma = 6917 \cdot 63$.   These differ from the corresponding ϕ terms in the expected direction towards $4\mathrm{R}/m^2$, but there is no line corresponding with the term 5γ, which would be about ν 15920.

It should also be mentioned that there is a possible " multi-doublet " in the extreme ultra-violet, formed from $\lambda\lambda$ 1197·79 (3), 1194 ·89 (5), 1193 ·62 (3), and 1190 ·80 (4). There is at present no experimental evidence as to the class to which these lines belong, but they form an isolated group, and the occurrence of the separation 287 suggests that

they may belong to Si II. The wave-numbers may be arranged as a $\pi\pi'$ combination in the following manner :—

$1\pi_1$		$1\pi_2$	
(2)		(1)	j
83487	*292*	83779	π'_2 (1)
203		*198*	
83690	*287*	83977	π'_1 (2)

The discordances between the separations, which might be expected to be equal, are within the limits of error of measurement in this region, and if the combination be significant, it results that $\pi'_1 = 47841$, $\pi'_2 = 48042$.

The highest term of Si II is a " p "-term, and on BOHR's theory the associated azimuthal or subordinate quantum number must therefore be 2. It thus appears that in the normal state of the ionised atom, and probably also in the neutral atom, the 13th electron moves in a 3_2 orbit.

The second ionisation potential of silicon, deduced from the above value of $1\pi_2$ in the usual manner, is 16·27 volts.

Comparison of Si II and Al I.

In accordance with the spectroscopic displacement law, it was to be expected that the series of Si II would be found to be generally similar to those of Al I. Both spectra are, in fact, constituted of doublets, and differ chiefly in the wider separation of the pairs in Si II, and in the displacement of lines of Si II to the region of much shorter wave-lengths as compared with corresponding lines of Al I. This, of course, is due to the greater charge of the " core," or " atomic residue," with respect to the series electron in the case of Si II as compared with that of Al I.

Comparison of Chief Lines.—Some of the corresponding lines of the two spectra are indicated in Table II.

TABLE II.—Comparison of Chief Lines of Si II and Al I.

Series.	Al I.	Si II.
	λ	λ
$1\pi_1 - 2\sigma$	3961·54	1533·55
$1\pi_2 - 2\sigma$	3944·03	1526·83
$1\pi_1 - 2\delta_2$	3092·84	—
$1\pi_1 - 2\delta_1$	3092·72	1265·04
$1\pi_2 - 2\delta_2$	3082·16	1260·66
$2\sigma - 2\pi_1$	21166	6347·09
$2\sigma - 2\pi_2$	21098	6371·36
$2\pi_1 - 3\delta_1$	16752	5056·02
$2\pi_2 - 3\delta_2$	16721	5041·06
$2\delta_1 - 3\phi$ $2\delta_2 - 3\phi$	11255	{ 4130·88 { 4128·05

E 2

The table illustrates very clearly how lines of Al I which occur in the near ultra-violet are represented in Si II by lines which appear in the Schumann region, while infra-red lines of Al I correspond with lines of Si II which occur in the visible spectrum.

The main doublet separations, $1\pi_2 - 1\pi_1$, are 112 for Al I and 287 for Si II, in the ratio $1 : 2 \cdot 56$.

Effective Quantum Numbers.—The values of the terms of Al I and Si II are most effectively compared for theoretical purposes by a statement of the effective quantum numbers; that is, of the values of $\sqrt{R/\text{term}}$ for Al I and of $\sqrt{4R/\text{term}}$ for Si II. These are given, with the BOHR numeration of terms, in Table III.

TABLE III.—Effective Quantum Numbers of Al I and Si II.

Bohr Numbers.	3	4	5	6	7
$m\sigma$ { Al I		2·186892	3·217954	4·227570	5·231357
{ Si II		2·571925	3·599996	4·610472	5·616184
$m\pi_2$ { Al I	1·507207	2·674639	3·700549	4·709045	
{ Si II	1·824328	2·943593	3·960963	4·968841	
$m\pi_1$ { Al I	1·508958	2·675967	3·701923	4·710388	
{ Si II	1·826318	2·945339	3·962685	4·970115	
$m\delta_1$ { Al I	2·631031	3·425462	4·260130	5·164510	
{ Si II	2·891673	3·774168	4·751900	5·743038	
$m\phi$ { Al I		3·968941	4·963713		
{ Si II		3·939695	4·928499	5·921808	

An important difference between the two spectra is the appearance in Si II of the strong series $x - 3\phi$, which has not been found in Al I.

Comparison of Si II and C II.

Elements belonging to the same sub-group of the periodic table exhibit certain progressive spectral differences with increase of atomic weight, or of atomic number,[*] and it is now possible to observe such relations in the spectra of the two ionised elements, silicon and carbon, the data for C II having already been communicated to the Society.[†]

It may be noted in the first place that the main doublet separations for Si II and C II, which are 287 and 58 respectively, follow the usual rule that the separations are roughly proportional to the squares of the atomic numbers, their ratio being $5 \cdot 0$ as compared with $5 \cdot 4$ from the atomic numbers 28 and 12. It also appears that the

[*] See FOWLER's "Report on Series," p. 43.
[†] 'Roy. Soc. Proc.,' vol. 105, p. 299 (1924).

two ionised elements follow the rule that the limits of the sharp and principal series (1π and 2σ, respectively) are displaced towards the red with increase of atomic number. This result is included in the general comparison of the spectral terms given in Table IV.

TABLE IV.—Spectral Terms of Si II and C II.

RYDBERG Numbers.	1	2	3	4	5
x C II		100165			
x_2 Si II		76514			
$m\sigma$ $\begin{cases} \text{C II} \\ \text{Si II} \end{cases}$		80121 / 66323	39425 / 33851	23311 / 20639	(15387) / 13909
$m\pi_2$ $\begin{cases} \text{C II} \\ \text{Si II} \end{cases}$	196670 / 131818	64934 / 50632	34140 / 27963	17769	
$m\delta_1$ $\begin{cases} \text{C II} \\ \text{Si II} \end{cases}$		51108 / 52466	28535 / 30800	18164 / 19429	(12558) / 13301
$m\phi$ $\begin{cases} \text{C II} \\ \text{Si II} \end{cases}$			27680 / 28265	17703 / 18061	12283 / 12510

It should be remarked also that the corresponding δ and ϕ terms increase in passing from C II to Si II, exactly as they do with increase of atomic number in the case of the alkali metals.

Although Si II resembles C II in having a term "x," it is important to note that whereas in Si II this term is definitely of δ type, it is apparently of σ type in C II.

VI. THE TRIPLETS AND SINGLETS OF SI III (SI^{++}).

General Remarks.

The third spectrum of silicon forms a triplet system, with its accompanying series of singlets, as in the spectra of the alkaline earths. One of the triplets, having its strongest line at $\lambda 4552$, is well known from its occurrence in the spark and in certain stellar spectra. A second triplet, having its strongest line at $\lambda 3806$, is also present in the spark, but the Si III spectrum as a whole is but feebly represented under spark conditions. The lines are much more completely revealed by the vacuum tube observations of silicon fluoride, and they appear under conditions of discharge which are consistent with their assignment to doubly-ionised silicon. As in Si II, the lines which appear in the ordinary region of observation with gratings or quartz spectrographs belong to secondary series. The chief members lie in the extreme ultra-violet and have only been partially observed. The author's observations include the triplet beginning at $\lambda 1113$, and for the first two members of the triplet beginning at $\lambda 997$ he is indebted to the photograph of the silicon vacuum arc placed at his disposal by Mr. SIMEON.

The lines which have been identified as belonging to the triplet system of Si III are collected in Table V and again in order of wave-length in Tables X and XIII.

The Triplet System of Si III.

Of the four triplets which have been observed in the ordinary range, two are inverted and must therefore be given negative signs in the calculation of limits. One of them, having its strongest line at λ 3086, is accompanied by satellites, and there is accordingly no difficulty in deciding as to the two triplets which belong to the diffuse series, although the satellites to the second triplet have not been resolved. The satellites observed are abnormal, inasmuch as they appear on the more refrangible (actually less refrangible because of the inversion) side of the chief lines ; in other words, $d_1 > d_2 > d_3$. The corresponding triplet in Al II, as observed by PASCHEN, is similarly inverted and has the same abnormality in connection with the satellites.

As only two members of the sharp and two of the diffuse series have been observed in the ordinary region, the data are inadequate for precise calculations of limits. The following RYDBERG formulæ, however, may be quoted as indicating the approximate limits :—

Second Diffuse series :—

$$\left.\begin{array}{l} 2p_3 - 2d_3 = -\ 32282 \cdot 21 \\ 2p_3 - 3d_3 = \ 26367 \cdot 96 \end{array}\right\} \quad \nu = 95459 \cdot 16 - 9R/(m + 0 \cdot 779813)^2.$$

Second Sharp series :—

$$\left.\begin{array}{l} 2p_3 - 2s = -\ 21852 \cdot 99 \\ 2p_3 - 3s = \ 30945 \cdot 58 \end{array}\right\} \quad \nu = 96070 \cdot 00 - 9R/(m + 0 \cdot 893226)^2.$$

These results are sufficient to show the order of magnitude of the term $2p_3$, and in view of the approximate character of the formulæ, the accordance of the two calculated limits provisionally serves to justify the assumption that the series constant for these triplets is 9R.

Taking $2p_3 = 96070$, and assuming the usual RYDBERG relations, the formulæ lead to λ 1340 as the approximate position of the leading triplet of the first diffuse series. The earlier photographs with the vacuum spectrograph, taken through a fluorite window, showed no such triplet in the region less refrangible than λ 1220, but later photographs of the vacuum arc, taken without window, revealed it at λ 1113. This triplet is more strongly shown in SIMEON's photograph and has also been recorded by MILLIKAN.

The triplet of the first sharp series has only been partially recorded. Its position with respect to the first diffuse triplet is accurately known from the fact that the interval separating the two is identical with that separating the triplets at λ 4552 and λ 3086. The triplet lies beyond the region photographed by the author, but the first two members appear near the limit of sensitivity on SIMEON's plate.

With the term $2d$ roughly determined from the above formulæ, and by assuming a value for the first f term, which is nearly the same for most series, it seemed probable that the first member of the fundamental series must be the complex line about $\lambda 1500$. It then became clear that a narrow triplet beginning at $\lambda 4829$ must belong to the fg, or super-fundamental, series and that a fainter triplet having its first line at $\lambda 3040$ was the second member of this series.

The last-named triplets appear to provide the most suitable means of fixing the limits of the various series. Not more than two members of any of the series have so far been observed, and the g terms may be expected to show the least departure from simple RYDBERG terms. We thus have

$$\left.\begin{array}{l} 3f_1 - 4g = 20702 \cdot 79 \\ 3f_1 - 5g = 32875 \cdot 14 \end{array}\right\} \quad \begin{array}{l} 3f_1 = 60444 \cdot 00 \\ \\ 3f_2 = 60483 \cdot 44 \\ \\ 3f_3 = 60511 \cdot 23 \end{array}$$

In view of the triple character of the f terms, as well as of the d terms, the line of the fundamental series near $\lambda 1500$ is a complex of six components. Owing to the small resolving power of the vacuum spectrograph, however, only three components have been observed. It may be supposed that one of these represents $2d_1 - 3f_1$, and the d_2 and d_3 terms may then be deduced by using the values of $\Delta\nu$ from the diffuse triplet at $\lambda 3086$. Thus :—

$$\begin{array}{ll} 2d_1 - 3f_1 = 66649 & 2d_1 = 127093 \cdot 00 \\ \quad\quad 3f_1 = 60444 & 2d_2 = 127090 \cdot 86 \\ & 2d_3 = 127088 \cdot 85 \end{array}$$

The possible df combinations may be most clearly indicated by making use of the inner quantum numbers (j), to which reference has already been made. Under ordinary conditions the permissible combinations are those of terms for which the values of j differ by unity or zero, with the exception that transitions $j = 0$ to $j' = 0$ do not usually occur. The df combinations are, therefore, as follow :—

Values of j.

$$\begin{array}{lll} d_1 f_1 = d_3 - f_4 = 66649 \cdot 00 & \text{(adapted to agree with observation).} \\[4pt] \left.\begin{array}{l} d_1 f_2 = d_3 - f_3 = 66609 \cdot 56 \\ d_2 f_2 = d_2 - f_3 = 66607 \cdot 42 \end{array}\right\} & \text{observed} = 66608. \\[8pt] \left.\begin{array}{l} d_1 f_3 = d_3 - f_2 = 66581 \cdot 77 \\ d_2 f_3 = d_2 - f_2 = 66579 \cdot 63 \\ d_3 f_3 = d_1 - f_2 = 66577 \cdot 62 \end{array}\right\} & \text{observed} = 66578. \end{array}$$

The values of the $2d$ terms above determined immediately lead to the terms $2p$ and $3d$, through the observed lines of the second diffuse series, and $2p$ then gives the values of the s terms with the aid of the observed lines of the second sharp series. The

terms $2p$ thus arrived at are in sufficient agreement with the approximate values previously calculated independently from the second sharp and diffuse series. The chief remaining terms, $1p$, have been derived from the first diffuse triplet at $\lambda\,1113$. All the results for the triplet system which are at present available are collected in Table V.

TABLE V.—Triplet Series of Si III.

1st Sharp Series.—$1p - ms$; $1p_1 = 216879$; $1p_2 = 217142$; $1p_3 = 217273$.

Observed.			Calculated.			$m\,(+2).$	ms
$\lambda.$	$\nu.$	$\Delta\nu.$	$\lambda.$	$\nu.$	$\Delta\nu.$		
$997\cdot70$	100230		$997\cdot81$	100219			
		249			263	(2)	116660
$995\cdot23$	100479		$995\cdot20$	100482			
					131		
—	—		$993\cdot91$	100613			

1st Diffuse Series.—$1p - md$; $1p_1 = 216879$; $1p_2 = 217142$; $1p_3 = 217273$.

Observed.			Calculated.	$m\,(+1).$	$md_1\ d_2\ d_3$
$\lambda.$	$\nu.$	$\Delta\nu.$			
$1113\cdot76$	89786				127093
		266	Used for calculation	(2)	
$1110\cdot47$	90052		of $1p$.		127091
		132			
$1108\cdot85$	90184				127089

Fundamental Series.—$2d - mf$; $2d_1 = 127093\cdot00$; $2d_2 = 127090\cdot86$; $2d_3 = 127088\cdot85$.

Observed.			Calculated.			$m\,(+1)$	$mf_1\ f_2\ f_3$
$\lambda.$	$\nu.$	$\Delta\nu.$	$\lambda.$	$\nu.$	Comb.		
$1500\cdot39$	66649		$*1500\cdot39$	$*66649\cdot00$	$d_1 f_1$		
		41					$\left\{\begin{array}{l}60444\cdot00\end{array}\right.$
$1501\cdot32$	66608		$\left\{\begin{array}{l}1501\cdot29\\1501\cdot34\end{array}\right.$	$\begin{array}{l}66609\cdot56\\66607\cdot42\end{array}$	$\begin{array}{l}d_1 f_2\\d_2 f_2\end{array}$	(3)	$60483\cdot44$
		30					$60511\cdot23$
$1502\cdot00$	66578		$\left\{\begin{array}{l}1501\cdot91\\1501\cdot96\\1502\cdot01\end{array}\right.$	$\begin{array}{l}66581\cdot77\\66579\cdot63\\66577\cdot62\end{array}$	$\begin{array}{l}d_1 f_3\\d_2 f_3\\d_3 f_3\end{array}$		
$1142\cdot74$?	87509				$d_1 f_1$		$\left\{\begin{array}{l}39584\ ?\end{array}\right.$
		161				(4)	$39744\ ?$
$1144\cdot85$?	87348				$d_{21} f_2$		
—	—				—		—

* Used for calculation of $2d_1$.

TABLE V (continued).

Principal Series.—$2s - mp$; $2s = 116659 \cdot 56$.

λ, Intensity.	ν.	$\Delta \nu$.	$m (+ 2)$.	$mp_1 \, p_2 \, p_3$.
—997·70	—100230	249	(1)	216890
—995·23	—100479	(134)		217139
—	—(100613)			217273
4552·654 (9)	21959·17	73·16	(2)	94700·39
4567·872 (7)	21886·01	33·02		94773·55
4574·777 (4)	21852·99			94806·57

2nd Sharp Series.—$2p - ms$; $2p_1 = 94700 \cdot 33$; $2p_2 = 94773 \cdot 54$; $2p_3 = 94806 \cdot 64$.

λ, Intensity.	ν.	$\Delta \nu$.	$m (+ 2)$.	ms.
—4552·654 (9)	—21959·17	73·16	(2)	116659·56
—4567·872 (7)	—21886·01	33·02		
—4574·777 (4)	—21852·99			
3241·67 (6)	30839·43	73·14	(3)	63861·01
3234·00 (5)	30912·57	33·01		
3230·55 (3)	30945·58			

2nd Diffuse Series.—$2p - md$; $2p_1 = 94700 \cdot 33$; $2p_2 = 94773 \cdot 54$; $2p_3 = 94806 \cdot 64$.

λ, Intensity.	ν.	$\Delta \nu$.	$m (+ 1)$.	$md_1 \, d_2 \, d_3$.
—3086·225 (7)	—32392·67	2·14	(2)	127093·00
—3086·429 (3)	—32390·53	2·02		127090·86
—3086·620 (0)	—32388·51			127088·85
—3093·423 (6)	—32317·31	73·21		
—3093·613 (3)	—32315·31	2·00		
—3096·786 (4)	—32282·21	33·10		
3806·56 (5)	26263·00	72·30	(3)	68438·08
3796·11 (4)	26335·30	32·66		
3791·41 (3)	26367·96			

$1S - 1p_2 = 39330$ $1S = 256472$.

TABLE V (continued).

Super-Fundamental Series.—$3f - mg$; $3f_1 = 60444 \cdot 00$; $3f_2 = 60483 \cdot 44$; $3f_3 = 60511 \cdot 23$.				
λ, Intensity.	ν.	$\Delta \nu$.	$m(+1)$.	mg.
4828·923 (4n) 4819·740 (3n) 4813·290 (2n)	20702·79 20742·23 20770·02	39·44 27·79	(4)	39741·21
3040·93 (1) 3037·26 (1) 3034·74 (1)	32875·14 32914·87 32942·20	39·73 27·33	(5)	27568·82

Six lines forming a pp' multiplet may be arranged as follows :—

$$
\begin{array}{cccccc}
1p_1 & & 1p_2 & & 1p_3 & \\
(2) & & (1) & & (0) & j \\
& & 76{,}845 & & & p'_3\ (0) \\
& & 131 & & & \\
76{,}712 & 264 & 76{,}976 & 133 & 77{,}109 & p'_2\ (1) \\
264\ . & & 263 & & & \\
76{,}976 & 263 & 77{,}239 & & & p'_1\ (2) \\
\end{array}
$$

$$p'_1 = 139{,}903 ; \quad p'_2 = 140{,}166 ; \quad p'_3 = 140{,}297$$

This group is well defined and confirms very closely the values of the main triplet separations already adopted. A similar multiplet appears in Al II, with its first line at λ 1767·6 ($\nu = 56574$), and in Mg I with the first line at λ 2783 ($\nu = 35922$).

The highest term of the triplet series is a p term, but a still higher term is to be expected in connection with the associated singlets, so that the p term in question gives no direct indication of the normal state of the doubly-ionised silicon atom.

Comparison of Triplets of Si III, Al II, and Mg I.

In accordance with the normal atomic numbers of the three elements a close similarity between the spectra of Si III, Al II and Mg I is to be expected. All three spectra do, in fact, include triplet systems in association with singlets. The three atoms in the states indicated by the symbols have the same number of external electrons, but the nuclei differ in mass and charge. The effect of mass is so small as to be negligible in the present discussion, but, as previously explained, the effect of increased nuclear charge is to displace the spectrum as a whole to the region of short wave-lengths.

Corresponding Lines.—Some of the chief corresponding lines of the triplet systems are indicated in Table VI.

TABLE VI.—Comparison of Chief Lines of Si III, Al II and Mg I.

—		Mg I.	Al II.	Si III.
1st sharp, $1p_1 - 2s$	λ	5183	1862	998
	ν	19286	53692	100230
2nd sharp, $2s - 2p_1$	λ	—	7042	4553
	ν	—	14196	21959
1st diffuse, $1p_1 - 2d_1$	λ	3838	1725	1114
	ν	26046	57970	89786
2nd diffuse, $2d_1 - 2p_1$ . . .	λ	—	10080	3086
	ν	—	9921	32393
Fundamental, $2d_1 - 3f_1$ . . .	λ	14877	3587	1500
	ν	6720	27874	66649

The Triplet Separations.—Increase of nuclear charge in similarly constituted atoms results in increased separations of the components of the triplets as shown in Table VII.

TABLE VII.—Triplet Separations of Si III, Al II and Mg I.

—		Mg I.	Al II.	Si III.
At. Wt.		$24 \cdot 32$	$27 \cdot 1$	$28 \cdot 3$
Nuclear charge		12	13	14
Charge of core (c)		1	2	3
Separations $\begin{cases} \Delta p_{21} \\ \Delta p_{32} \end{cases}$	Δp_{21}	$40 \cdot 9$	$125 \cdot 5$	263
	Δp_{32}	$19 \cdot 9$	$61 \cdot 8$	131

A striking result of the comparison is that the ratio of the two separations of the respective triplets is practically constant and equal to 2 : 1. Further, there is a nearly linear relation between the separations and the squares of the residual charges. Thus, the equation

$$\Delta \nu = 13 + 28c^2$$

gives the values 41, 125, 265 for Mg I, Al II and Si III respectively, and it may be observed that there is an uncertainty of a few units in the tabulated value for Si III, as it depends upon measurements in the extreme ultra-violet. The separations are, therefore, much more simply related than those of successive elements belonging to

the same group of the periodic table. This has also been noted in the previous paper on Si IV.

Effective Quantum Numbers.—In the comparison of the effective quantum numbers of Si III, Al II and Mg I (Table VIII), the numbers represent $\sqrt{9R/\text{term}}$, $\sqrt{4R/\text{term}}$ and $\sqrt{R/\text{term}}$ respectively. For Al II the value of R has been taken as $109734 \cdot 98$ as adopted by PASCHEN for this spectrum. For the other elements $R = 109678 \cdot 3$.

TABLE VIII.—Effective Quantum Numbers of Si III, Al II, and Mg I.

Bohr numbers.	3.	4.	5.	6.
ms { Mg I Al II Si III		$2 \cdot 314482$ $2 \cdot 691566$ $2 \cdot 908850$	$3 \cdot 345514$ $3 \cdot 716978$ $3 \cdot 931549$	
mp_1 { Mg I Al II Si III	$1 \cdot 660865$ $1 \cdot 959816$ $2 \cdot 133402$	$2 \cdot 817126$ $3 \cdot 075940$ $3 \cdot 228536$		
md_1 { Mg I Al II Si III	$2 \cdot 827920$ $2 \cdot 791874$ $2 \cdot 786896$	$3 \cdot 829341$ $3 \cdot 801090$ $3 \cdot 797805$		
mf_1 { Mg I Al II Si III		$3 \cdot 959795$ $3 \cdot 928628$ $4 \cdot 041150$	$4 \cdot 953992$ $4 \cdot 882470$ $4 \cdot 993692$?	
mg { Mg I Al II Si III			— $4 \cdot 982972$ $4 \cdot 983806$	— $5 \cdot 980675$ $5 \cdot 983737$

The Singlets of Si III.

There are numerous lines which are developed in the silicon spectrum simultaneously, or nearly so, with the triplets of Si III, and many of them doubtless belong to the associated singlet system. The arrangement of these in series has not yet been finally accomplished, and may not be possible until improved observations in the region beyond λ 1200 have been obtained. The identification of the resonance line, $1S - 1p_2$, and of the first line of the principal series, $1S - 1P$, however, can be made with reasonable certainty.

Considerable assistance might be expected from comparisons with the singlet series of Mg I and Al II. Those of Mg I are well known, but those of Al II are unfortunately not yet fully established. PASCHEN has not published any singlet series for Al II, but H. N. RUSSELL* has attempted to trace the leading members of the four series from

* ' Nature,' vol. 113, p. 163 (1924).

PASCHEN'S data. RUSSELL's method was to form ratios of corresponding s, p, d terms of Al II and Mg I, and to plot these ratios against the known terms of Mg I. Then, from the known S, P, D terms of Mg I the ratio of the singlet terms of Al II and Mg I were obtained by interpolation. The rough values of the singlet terms thus obtained suggested the allocation of some of the lines of Al II.

Only two members of each of the triplet series have been observed in Si III, and RUSSELL's method therefore becomes merely a linear interpolation or extrapolation in this case. It is, nevertheless, worth while to see how far the method is applicable. The relevant data and the results are as follows :—

	Al II.	Si III.	Ratio.		Al II.	Si III.	Ratio.
$2s$ . .	60589	116660	1·926	1S . .	147107	(246200)	(1·674)
$1p_1$.	114281	216904	1·898	1P . .	87262	(170600)	(1·954)
$2p_1$.	46393	94700	2·041	2P . .	43759	(89580)	(2·046)

The interpolated ratios and singlet terms for Si III are shown in brackets. The value for 1S involves a long extrapolation and may be much in error.

It is possible that more exact values, assuming the method of ratios to be valid, may be obtained by plotting the logarithms of the ratios against the logarithms of the terms. This procedure gives 1S = 267000, 2S = 105600, 1P = 169200, 2P = 89740.

The most appropriate line for 1S — 1P in any reasonable accordance with the above calculations is that at λ 1206·9 (ν = 82857) ; this is by far the strongest singlet in the range λ 1400 — λ 990, and may be adopted with considerable confidence.

For the identification of the resonance line 1 S — 1 p_2 we have 1 p_2 = 217140, and the above calculated values of 1 S give the wave-numbers 29060 and 49860. The limits are wide, but there are no strong singlets near this range except λ 3590 (ν = 27844), λ 3486 (ν = 28670), λ 2559 (ν = 39063), and λ 2541 (ν = 39330). Of these, there can be little hesitation in selecting the last as the most probable resonance line. Its physical behaviour is precisely in accordance with this view, as it is more strongly developed in the ordinary spark than any of the other lines, just as the resonance line of Al II suggested by RUSSELL makes its appearance in the arc, and that of Mg I in the flame.

The identification of the resonance line, and the consequent deduction as to the third ionisation potential, is of considerable importance for astrophysical investigations, and further checks on the line adopted may accordingly be mentioned. If the logarithms of the values of 1S — $1p_2$ be plotted against the logarithms of the $1p_2$ terms for Mg I, Al II and Si III, the value of 1S — $1p_2$ for Si III is given as ν = 41700, which is in sufficient agreement with the adopted line ν = 39330. A similar procedure gives 1S — 1P for Si III = 83000, almost in exact agreement with the adopted line 82857.

Again, if the resonance lines of Na I, Mg II, Al III and Si IV be plotted against the corresponding nuclear charges, or numbers increasing by unity, the points lie very nearly

on a straight line. If a similar relation holds for Mg I, Al II, Si III, the value of $1S - 1p_2$ for Si III will be less than 43530, as will appear from the data given below.

	$1\sigma - 1\pi$.	$\Delta\nu$.		$1S - 1p_2$.	$\Delta\nu$.
Na I	16973		Mg I	21870	
		18788			10830
Mg II	35761		Al II	32700	
		18157			
Al III	53918		Si III	(< 43530)	
		17822			
Si IV	71740				

Thus, although it is not to be considered as fully established, there are substantial grounds for the adoption of ν 82857 as the $1S - 1P$ line, and of ν 39330 as the $1S - 1p_2$ line of Si III. If the identification be correct, the terms 1 S and 1 P may then be deduced as follows :—

$$1S - 1p_2 = 39330$$
$$1p_2 = 217142$$
$$256472 = 1\,S$$
$$1S - 1P = 82857$$
$$173615 = 1P$$

Plausible assignments of other lines of the singlet series might be made, but it is considered desirable to defer the further discussion until more complete silicon data are available for the extreme ultra-violet, and it becomes possible to derive further assistance from the singlet series of Al II.

The above values for $1S - 1p_2$ and $1S$ suggest that the resonance and ionisation potentials of Si III are respectively 4·85 volts and 31·66 volts, but these values cannot yet be considered final.

There can be no doubt, however, that the spectrum of Si III is generally similar to the spectra of Al II and Mg I, consisting of singlets and triplets, and having 1S for the largest term. As in Al II and Mg I, it may accordingly be concluded that the series electron in Si III normally occupies a 3_1 orbit.

VII. The Series System of Si IV (Si^{+++}).

Details of the observations and analysis of the spectrum of Si IV having already been communicated to the Society,* it is only necessary to summarise the chief results for convenient comparison with the spectra at other stages of ionisation.

The constant for the series was definitely proved to be 16R, in accordance with Bohr's theory, and the whole system was shown to be similar in structure to the doublet

* *Loc. cit.*

series of Al III, Mg II, and Na I, for which the series constants are respectively 9R, 4R, and R. With increase in the value of the series constant, however, the spectrum is displaced as a whole towards shorter wave-lengths. Thus, the brighter component of the first principal pair of lines in Na I is at $\lambda 5889 \cdot 9$, in Mg II at $\lambda 2795 \cdot 5$, in Al III at $1854 \cdot 7$, and in Si IV at $\lambda 1393 \cdot 9$. The chief series of Si IV lie in the extreme ultra-violet, those which appear in the ordinary range of observation being secondary series such as occur in the far infra-red in Na I.

It may also be noted that the separations $\Delta \nu$ of the first principal pairs are $17 \cdot 88$ for Na I, $91 \cdot 55$ for Mg II, 238 for Al III, and 460 for Si IV.

The various spectral terms of Si IV, with the notation of the present paper, are given in Table IX, calculated terms being enclosed in brackets.

TABLE IX.—The Series Terms of Si IV.

Rydberg Numbers.	σ.	π_2.	π_1.	δ.	ϕ.	γ.	κ.	Bohr Numbers.
1	364117	292837	292377					3
2	170105	145817	145655	203705				4
3	98666	87580	87505	114076	109923			5
4	[64401]	[58438]	[58397]	72594	70366	70213		6
5	[45319]	[41766]	[41741]	[50186]	48862	48788	48733	7
6	[33638]	[31335]	[31319]	[36741]	35893	35835	[35800]	8
7				[28050]	[27476]			

The largest term is the 1σ term, from which it follows that the series electron in Si IV normally occupies a 3_1 orbit, as in Al III, Mg II, and Na I. The corresponding ionisation potential of Si IV, representing the energy required to expel the fourth of the outermost electrons from the silicon atom when three of them have already been removed, is $44 \cdot 95$ volts.

The lines of Si IV which have been classified in series are included in Tables X and XIII. The positions of several lines as calculated from the series terms given in Table IX have been included, and it will be seen that nearly all of these have since been confirmed by the observations of BOWEN and MILLIKAN* or of MCLENNAN and SHAVER.†

VIII. GENERAL CONCLUSIONS.

(1) The investigation has shown that the changes in the spectrum of silicon which accompany appropriate increases in the energy of the exciting source represent successive

* ' Phys. Review,' vol. 23, p. 1 (1924).
† ' Trans. Roy. Soc. Canada,' vol. 18, p. 1 (1924).

ionisations of the silicon atom. This has been established through the identification of four successive systems of spectral series, which are respectively characterised by the series constants R, 4R, 9R and 16R, in accordance with the theory of BOHR.

(2) The spectrum of the neutral atoms (Si I) includes singlets and triplets. The singlets include PS and PD series, which have a common limit about 60072. Only one ps and one pd triplet have been certainly identified, and the triplet limits are not yet satisfactorily determined. There is no reasonable doubt, however, that the largest term of the spectrum is a p or P term, and it is concluded that the series electron normally moves in a 3_2 orbit. The ionisation potential cannot be less than $7 \cdot 5$ volts.

(3) The spectrum of singly-ionised atoms (Si II, or Si$^+$) includes a doublet system analogous with that of neutral aluminium. Lines at $\lambda\lambda$ 1533·55, 1526·83 ($\nu\nu$ 65208, 65495) form the leading pair of the sharp series, the limits of which are 131531 and 131818. The resonance potential is therefore $8 \cdot 09$ volts and the second ionisation potential $16 \cdot 27$ volts. Besides the usual sets of terms, there is a double term of d type, $x_1 = 76498$, $x_2 = 76514$, which yields a strong series of fundamental type in the far ultra-violet; no corresponding terms have been noted in aluminium. The largest term is a π term, and on BOHR's theory it follows that the series electron in Si II normally occupies a 3_2 orbit.

(4) The spectrum of doubly-ionised silicon (Si III or Si^{++}) is of the same type as that of Al II or Mg I, including triplets and singlets. The limits of the triplet series are 216879, 217142, and 217273. The singlet series have not yet been certainly traced, but there is evidence that the resonance line, $1S - 1p_2$, is ν 39330, while the first principal line, $1S - 1P$, is ν 82857. If so, the resonance potential would be $4 \cdot 85$ volts, and the ionisation potential $31 \cdot 66$ volts. As the largest term is 1S it may be concluded that the series electron normally traverses a 3_1 orbit, as in Mg I.

(5) The spectrum of trebly-ionised silicon (Si IV, or Si^{+++}), as shown in a previous paper, forms a doublet system similar to that of Al III, Mg II, and Na I. The leading pair of lines, corresponding with the " D " lines of neutral sodium, is formed by $\lambda\lambda$ 1393·9, 1402·9. Some of the series of Si IV which appear within the range of observation with ordinary instruments correspond with lines which occur in the far infra-red in neutral sodium. The resonance and ionisation potentials deduced from the observed series are respectively $8 \cdot 86$ and $44 \cdot 95$ volts. The series electron in Si IV normally moves in a 3_1 orbit.

TABLE X.—General Catalogue of Silicon Lines in the Region λ 6700 — λ 2000.

Wave-lengths, Intensities and Groups.				Wave-Numbers.	Series.
Si I	Si II.	Si III.	Si IV.		
	6671·88 (3)			14984·15	
	6660·49 (2)			15009·77	
	6371·359 (8)			15690·90	II $2\sigma - 2\pi_2$
	6347·091 (10)			15750·90	II $2\sigma - 2\pi_1$
	5978·970 (7)			16720·63	II $2\pi_1 - 3\sigma$
	5957·612 (5)			16780·61	II $2\pi_2 - 3\sigma$
5948·548 (5)				16806·18	
	5915·266 (1)			16900·74	
	5868·404 (3)			17035·70	
	5867·497 (1)			17038·38	
	5846·12 (0)			17100·63	
	5827·80 (0)			17154·38	
	5806·75 (2)			17216·57	
	5800·48 (1)			17235·19	
5797·855 (3)				17242·98	
	5794·58 (0)			17252·73	
5793·070 (3)				17257·23	
	5785·64 (1)			17279·39	
5780·378 (1)				17295·12	
5772·142 (2)				17319·80	
		5739·762 (8)		17417·51	
5708·400 (5)				17513·19	
	5706·375 (1)			17519·41	
	5701·375 (1)			17534·77	
5701·101 (1)				17535·61	
5690·424 (2)				17568·52	
	5688·856 (2)			17573·37	
5684·488 (3)				17586·87	
	5669·590 (4)			17633·07	
5665·554 (1)				17645·64	
	5660·72 (0)			17660·71	
5645·609 (2)				17707·97	
	5639·492 (2)			17727·18	
	5633·00 (0)			17747·61	
	5576·61 (1)			17927·07	
	5540·74 (0)			18043·14	
	5496·24 (1)			18189·21	
	5473·09 (0)			18266·15	
	5468·92 (2)			18280·08	
	5466·93 (0)			18286·73	
	5456·11 (2)			18322·99	
	5454·43 (0)			18328·63	
	5447·10 (0)			18353·31	
	5438·41 (1)			18382·63	
	5432·63 (0)			18402·19	
	5428·73 (0)			18415·41	
	5405·06 (0)			18496·05	
	5294·97 (1)			18880·61	
	5202·51 (3)			19216·15	
	5192·75 (1)			19252·27	
	5185·09 (1)			19280·72	
	5181·77 (1)			19293·07	

TABLE X (continued).

Si I.	Si II.	Si III.	Si IV.	Wave Numbers.	Series.
	5056·353 (2)			19771·60	II $2\pi_1 - 3\delta_2$
	5056·020 (10)			19772·90	II $2\pi_1 - 3\delta_1$
	5041·063 (8)			19831·58	II $2\pi_2 - 3\delta_2$
	4921·69 (1)			20312·57	
	4906·88 (1n)			20373·87	
	4882·98 (0n)			20473·59	
	4859·28 (1)			20573·45	
		4828·923 (4n)		20702·79	III $3f_1 - 4g$
		4819·740 (3n)		20742·23	III $3f_2 - 4g$
		4813·290 (2n)		20770·02	III $3f_3 - 4g$
		4716·658 (5)		21195·99	
		4683·774 (2)		21344·35	
	4683·018 (2)			21347·79	
		4665·87 (0)		21426·25	
	4656·80 (1)			21467·97	
			4654·14 (4n)	21480·25	IV $4\gamma - 5\kappa$
			4631·38 (3n)	21585·80	IV $4\phi - 5\gamma$
		4574·777 (4)		21852·99	III $2s - 2p_3$
		4567·872 (7)		21886·01	III $2s - 2p_2$
		4552·654 (9)		21959·17	III $2s - 2p_1$
			4212·44 (3)	23732·43	IV $4\delta - 5\phi$
	4198·174 (2)			23813·18	
	4190·738 (3)			23855·46	
	4130·884 (10)			24201·08	II $2\delta_1 - 3\phi$
	4128·053 (8)			24217·69	II $2\delta_2 - 3\phi$
			4116·104 (8)	24287·99	IV $2\sigma - 2\pi_2$
4102·945 (5)				24365·89	
			4088·863 (10)	24449·80	IV $2\sigma - 2\pi_1$
	4076·78 (1)			24522·27	
	4075·45 (2)			24530·27	
	4016·22 (0n)			24892·02	
	3998·00 (1n)			25005·46	
	3991·77 (2n)			25044·48	
	3977·46 (0n)			25134·59	
		3924·44 (4)		25474·15	
3905·515 (10)				25597·61	
	3862·592 (6)			25882·04	II $mx_2 - 2\pi_2$
	3856·021 (8)			25926·14	II $mx_1 - 2\pi_1$
	3853·657 (3)			25942·05	II $mx_2 - 2\pi_1$
		3806·56 (5)		26263·00	III $2p_1 - 3d_{321}$
		3796·11 (4)		26335·30	III $2p_2 - 3d_{32}$
		3791·41 (3)		26367·96	III $2p_3 - 3d_3$
			3773·13 (3)	26495·69	IV $3\delta - 3\pi_2$
			3762·41 (4)	26571·18	IV $3\delta - 3\pi_1$
		3590·46 (8)		27843·66	
		3486·93 (6)		28670·36	
		3482·70 (0n)		28705·2	
	3339·84 (3)			29932·98	II $2\pi_1 - 4\sigma$
	3333·16 (2)			29992·96	II $2\pi_2 - 4\sigma$
		3241·67 (6)		30839·43	III $2p_1 - 3s$
		3234·00 (5)		30912·57	III $2p_2 - 3s$

TABLE X (continued).

Wave-lengths, Intensities and Groups.				Wave-Numbers.	Series.
Si I.	Si II.	Si III.	Si IV.		
		3230·55 (3)		30945·58	III $2p_3 - 3s$
		3210·52 (3)		31138·64	
	3210·04 (3)			31143·30	II $2\pi_1 - 4\delta_{21}$
	3203·89 (2)			31203·07	II $2\pi_2 - 4\delta_2$
	3199·54 (1)			31245·48	
		3196·50 (3)		31275·20	
	3195·40 (0)			31285·96	
	3193·10 (1)			31308·50	
	3188·95 (1)			31349·25	
		3186·01 (2)		31378·18	
		3185·16 (3)		31386·55	
			3165·72 (8)	31579·28	IV $2\pi_1 - 3\delta$
			3161·63 (1)	31620·13	
			3149·56 (6)	31741·30	IV $2\pi_2 - 3\delta$
		3096·786 (4)		32282·21	III $2d_3 - 2p_3$
		3093·613 (3)		32315·31	III $2d_3 - 2p_2$
		3093·423 (6)		32317·31	III $2d_2 - 2p_2$
		3086·620 (1)		32388·51	III $2d_3 - 2p_1$
		3086·429 (3)		32390·53	III $2d_2 - 2p_1$
		3086·225 (7)		32392·67	III $2d_1 - 2p_1$
		3040·93 (1)		32875·14	III $3f_1 - 5g$
		3037·26 (1)		32914·87	III $3f_2 - 5g$
		3034·74 (1)		32942·20	III $3f_3 - 5g$
3020·01 (0)				33102·85	
2987·650 (5)				33461·39	
2970·35 (2)				33656·27	
	2905·70 (3)			34405·06	II $2\delta_1 - 4\phi$
	2904·29 (2)			34421·75	II $2\delta_2 - 4\phi$
			2895·13 (1)	34530·67	IV $4\phi - 6\gamma$
			2887·90 (1)	34617·11	
2881·585 (10R)				34692·97	I $1P - 1S$
	2726·74 (2)			36662·99	II $2\pi_1 - 5\sigma$
			2723·81 (1)	36702·30	IV $4\delta - 6\phi$
	2722·29 (1)			36722·91	II $2\pi_2 - 5\sigma$
	2682·27 (2)			37270·80	II $2\pi_1 - 5\delta_{21}$
	2677·98 (1)			37330·50	II $2\pi_2 - 5\delta_2$
			2675·26 (3)	37368·45	
		2659·84 (1)		37585·09	
		2655·87 (2)		37641·26	
			2655·58 (2)	37645·37	
		2640·80 (4)		37856·05	
2631·296 (5)				37992·77	
	2606·09 (1)			38360·21	II $2\sigma - 3\pi_2$
	2604·44 (2)			38384·52	II $2\sigma - 3\pi_1$
2568·66 (2)				38919·15	
		2559·22 (7)		39062·70	
		2546·10 (3)		39263·98	
		2541·83 (10)		39329·92	
2532·39 (2)				39476·52	
2528·516 (10R)				39537·01	I $1p_1 - 1p_2'$
2524·118 (9R)				39605·89	I $1p_2 - 1p_3'$
2519·210 (8R)				39683·03	I $1p_2 - 1p_2'$

TABLE X (continued).

Wave-lengths, Intensities and Groups.				Wave-Numbers.	Series.
Si I.	Si II.	Si III.	Si IV.		
			2517·56 (5)	39709·04	IV$\Big\}3\phi - 4\gamma$
			2517·48 (5)	39710·30	IV
2516·123 (15R)				39731·73	I $1p_1 - 1p_1'$
2514·331 (7R)				39760·04	I $1p_3 - 1p_2'$
2506·904 (10R)				39877·83	I $1p_2 - 1p_1'$
	2505·07 (0)			39907·01	
	2504·32 (1)			39918·97	
	2501·99 (1)			39956·15	II $2\delta_1 - 5\phi$
	2500·96 (1)			39972·60	II $2\delta_2 - 5\phi$
2452·136 (3)				40768·42	I $1p_1 - 2s$
		2449·53 (2n)		40811·79	
2443·378 (3)				40914·54	I $1p_2 - 2s$
2438·782 (3)				40991·64	I $1p_3 - 2s$
2435·159 (8R)				41052·61	I 1P — 1D
		2374·29 (1)		42104·97	
			2371·04 (1)	42162·69	
		2367·00 (1)		42234·65	
		2357·94 (2)		42396·91	
		2357·15 (2)		42411·12	
		2356·25 (3)		42426·77	
		2353·07 (1)		42484·65	
		2350·16 (1)		42537·26	
		2308·18		43310·83	
2303·06 (2)				43407·11	
			2300·90 (0)	43447·85	
			2287·08 (10d)	43710·37	IV $3\delta - 4\phi$
2218·917 (1)				45052·96	I $1p_1 - 2d_3$
2218·080 (2)				45069·96	I $1p_1 - 2d_2$
2216·685 (4)				45098·32	I $1p_1 - 2d_1$
2211·750 (2)				45198·92	I $1p_2 - 2d_3$
2210·912 (3)				45216·07	I $1p_2 - 2d_2$
2207·980 (2)				45276·09	I $1p_3 - 2d_3$
	2136·41 (1)			46792·69	
			2127·48 (4)	46989·05	IV $2\pi_1 - 3\sigma$
2124·140 (6R)				47062·94	I 1P — 2S
2123·070 (1)				47086·65	
			2120·19 (3)	47150·62	IV. $2\pi_2 - 3\sigma$
2084·48 (1)				47958·25	
2082·31 (0)				48008·23	
	2072·61 (10)			48232·89	II $mx_1 - 3\phi$
	2071·94 (8)			48248·49	II $mx_2 - 3\phi$
2065·57 (0)				48397·26	
2061·25 (1)				48498·67	
	2058·917 (0)			48553·61	II $2\sigma - 4\pi_2$
	2058·532 (1)			48562·70	II $2\sigma - 4\pi_1$
2058·20 (5R)				48570·51	I 1P — 2D
2054·85 (1)				48649·70	

TABLE XI.—Silicon Lines of Uncertain Groups in the Region λ 6700 — λ 2000.

Si III ?		Si IV ?	
λ, Intensity.	ν.	λ, Intensity.	ν.
4638·12 (1)	21554·44	3622·44 (0)	27597·86
4338·52 (1)	23042·88	3612·26 (1)	27675·63
4183·48 (0)	23896·83	3601·52 (2)	27758·16
3147·38 (0)	31763·28	3525·90 (2)	28353·48
3126·25 (0)	31977·97	3279·25 (0)	30486·02
3077·56 (00)	32483·87	3276·25 (1)	30513·93
3053·18 (1)	32743·25	3258·67 (1)	30678·55
3045·10 (0)	32830·13	3254·79 (00)	30715·11
3043·97 (0)	32842·31	3253·44 (00)	30727·85
3030·00 (0)	32993·73	3216·26 (1)	31083·06
2360·58 (1)	42349·50	3214·65 (0)	31098·63
2360·21 (1)	42356·14	2831·51 (1)	35306·48
2334·60 (1)	42820·73	2817·09 (1)	35487·19
2334·40 (1)	42824·40	2816·15 (1)	35499·04
		2365·05 (0)	42269·47
		2364·34 (0)	42282·16
		2349·51 (1)	42549·03

TABLE XII.—Arc Lines of Silicon (Si I) in the Region λ 2000 — λ 1840.

λ, Intensity.	ν.	Series.	λ, Intensity.	ν.	Series.
1991·80 (1)	50205·8		1901·00 (5R)	52603·9	I 1P — 3S
1988·97 (4)	50277·3	I $1p_1 - 1p_1''$	1892·80 (3R)	52831·8	I 1P — 3D
1986·33 (2)	50344·1	I $1p_1 - 1p_2''$	1881·60 (2)	53146·3	
1983·20 (3)	50423·6	I $1p_2 - 1p_1''$	1880·71 (1)	53171·4	I $1p_1 - 3s$?
1980·56 (2)	50490·8	I $1p_2 - 1p_2''$	1875·54 (2)	53318·0	I $1p_2 - 3s$?
1979·15 (2)	50526·7	I $1p_2 - 1p_3''$	1874·68 (3)	53343·9	
1977·54 (3)	50567·9	I $1p_3 - 1p_2''$	1872·87 (2)	53394·0	I $1p_3 - 3s$?
1962·80 (0)	50947·6		1852·50 (2)	53981·1	
1961·80 (1)	50973·6		1850·84 (1d?)	54029·5	
1961·00 (0)	50994·4		1850·07 (00)	54052·0	
1959·92 (1)	51022·5		1848·68 (0)	54092·7	
1958·40 (0)	51062·1		1847·95 (00)	54114·0	
1957·60 (1)	51083·0		1846·05 (00)	54169·7	
1954·71 (2)	51158·5		1845·57 (1n)	54183·8	
1946·64 (1)	51370·6		1843·70 (0)	54238·8	Ca ?
1940·33 (0)	51537·6		1841·25 (1n)	54310·9	
1904·30 (2)	52512·7				

TABLE XIII.—Classified Lines of Si II, Si III, and Si IV in the Region more Refrangible than λ 2000.

Si II.	Si III.	Si IV.	Wave-numbers.	Series.	B. & M.*	McL. & S.†
1817·06 (10)			55034	II $1\pi_1 - x_{12}$		1817·1 (10)
1808·14 (8)			55305	II $1\pi_2 - x_2$		1808·1 (10)
		1797·5 (0)	55633	IV $3\delta - 4\pi_2$		
		1796·1 (1)	55676	IV $3\delta - 4\pi_1$		
		1727·4 (4)	57888	IV $2\pi_2 - 2\delta$		1727·5 (3)
		1722·7 (5)	58050	IV $2\pi_1 - 2\delta$		1722·7 (4)
1711·0 ($6d$?)			58445	II $x_{12} - 4\phi$		
1563·1 ($3d$?)			63975	II $x_{12} - 5\phi$		
		1533·55	65208	IV $3\delta - 5\phi$		
1533·55 (10)			65208	II $1\pi_1 - 2\sigma$	1533·4 (0)	1533·5 (5)
1526·38 (8)			65495	II $1\pi_2 - 2\sigma$	1526·9 (0)	1526·8 (4)
	1502·00 (5)		66578	III $2d_{123} - 3f_3$		1502·0 (5)
	1501·32 (5)		66608	III $2d_{12} - 3f_2$		1501·3 (5)
	1500·39 (5)		66649	III $2d_1 - 3f_1$		1500·3 (5)
1485·4 (3)			67322	II $x_{12} - 6\phi$		
1438·9 (1)			69498	II $x_{12} - 7\phi$		
1408·8 (0)			70982	II $x_{12} - 8\phi$		
		1402·9 (8)	71280	IV $1\sigma - 1\pi_2$	1403·0 (6)	1402·7 (10)
		1393·9 (10)	71740	IV $1\sigma - 1\pi_1$	1393·9 (6)	1393·6 (10)
		[1368·72]‡	[73061]	IV $2\pi_1 - 4\delta$		1369·1 (1)
		[1365·69]	[73223]	IV $2\pi_2 - 4\delta$		1365·0 (2)
	1303·57 (2)		76712	III $1p_2 - p'_2$	1303·5 (1)	1303·3 (6)
	1301·32 (2)		76845	III $1p_2 - p'_3$		1301·2 (6)
	1299·10 (4)		76976	III $\begin{cases}1p_2 - p'_2 \\ 1p_1 - p'_1\end{cases}$	1299·0 (2)	1298·9 (7)
	1296·86 (2)		77109	III $1p_3 - p'_2$		
	1294·69 (2)		77239	III $1p_2 - p'_1$	1294·9 (1)	1294·5 (6)
		[1279·05]	78183	IV $3\delta - 6\phi$		
1265·04 (10)			79040	II $1\pi_1 - 2\delta_{12}$	1264·9 (1)	1264·7 (6)
1260·66 (8)			79324	II $1\pi_2 - 2\delta_2$	1260·5 (1)	1260·4 (5)
		[1230·71]	[81254]	IV $2\pi_1 - 4\sigma$		
		[1228·26]	[81416]	IV $2\pi_2 - 4\sigma$	1228·1 (0)	1227·7 (3)
		[1211·75]	[82525]	IV $2\sigma - 3\pi_2$		
		[1210·65]	[82600]	IV $2\sigma - 3\pi_1$		1210·5 (3)
	1206·9 (10)		82857	III 1S — 1P	1206·5 (5)	1206·6 (10)
1197·79 (3)			83487	II $1\pi_1 - 2\pi'_2$		
1194·89 (5)			83690	II $1\pi_1 - 2\pi'_1$	1194·4 (0)	
1193·62 (3)			83779	II $1\pi_2 - 2\pi'_2$		
1190·80 (4)			83977	II $1\pi_2 - 2\pi'_1$		
		[1154·73]	[86600]	IV $3\delta - 7\phi$		1154·5 (0)
	1144·85 (1)		87348	III $2d_1 - 4f_1$?		1144·8 (2)
	1142·74 (0)		87509	III $2d_{12} - 4f_2$?		
		[1127·75]	[88672]	IV $1\pi_1 - 2\delta$	1128·4 (2)	1128·1 (8)
		[1121·93]	[89132]	IV $1\pi_2 - 2\delta$	1122·6 (2)	1122·2 (8)
	1113·76 (5)		89786	III $1p_1 - 2d$	1113·5 (2)	1113·0 (8)
	1110·47 (5)	.	90052	III $1p_2 - 2d$	1110·3 (2)	1109·7 (7)
	1108·85 (4)		90184	III $1p_3 - 2d.$	1108·9 (2)	1108·2 (6)

* BOWEN and MILLIKAN, *loc. cit.*   † McLENNAN and SHAVER, *loc. cit.*
‡ Figures in brackets represent calculated lines.

TABLE XIII (continued).

λ vac. and Groups.			Wave-numbers.	Series.	Other observations.	
Si II.	Si III.	Si IV.			B. & M.	McL. & S.
		1066·3 (8)*	93782	IV $2\delta - 3\phi$	1066·7 (0)	1066·4 (8)
[1023·75]			[97680]	II $1\pi_1 - 3\sigma$		
[1020·75]			[97967]	II $1\pi_2 - 3\sigma$		
	997·70 (1)		100230	III $1p_1 - 2s$	997·5 (0)	997·4 (4)
	995·23 (0)		100479	III $1p_2 - 2s$	994·6 (0)	994·7 (4)
	[993·94]		[100610]	III $1p_3 - 2s$		
993·09 (1)			100696	II $1\pi_1 - 3\delta_{12}$		
990·32 (0)			100977	II $1\pi_2 - 3\delta_2$		
		[859·52]	[111667]	IV $2\sigma - 4\pi_2$		
		[859·25]	[111708]	IV $2\sigma - 4\pi_1$		
		[817·85]	[122272]	IV $1\pi_1 - 2\sigma$	818·0 (2)	818·0 (7)
		[814·78]	[122732]	IV $1\pi_2 - 2\sigma$	815·0 (2)	814·8 (7)
		[779·19]	[128339]	IV $2\sigma - 5\pi_2$		} 778·7 (0)
		[779·03]	[128364]	IV $2\sigma - 5\pi_1$		
		[749·97]	[133339]	IV $2\delta - 4\phi$		749·7 (3)
		[645·82]	[154843]	IV $2\delta - 5\phi$		646·0 (1)
		[560·85]	[178301]	IV $1\pi_1 - 3\delta$		} 561·1 (1)
		[559·41]	[178761]	IV $1\pi_2 - 3\delta$		
		[458·09]	[218300]	IV $1\sigma - 2\pi_2$	} 457·7 (3)	457·8 (0)
		[457·75]	[218462]	IV $1\sigma - 2\pi_1$		
		[361·615]	[276537]	IV $1\sigma - 3\pi_2$	} 361·6 (1)	
		[361·517]	[276612]	IV $1\sigma - 3\pi_1$		

* This line does not occur in the vacuum arc; it was originally adopted from Millikan's observations of the vacuum spark of carbon.

Description of Plates.

The photographs which are reproduced are mainly intended to illustrate progressive changes in the spectrum of silicon, as observed in vacuum tubes of silicon tetrafluoride with discharges of varying intensity. In each set of spectra the effect of a comparatively feeble discharge is shown at the bottom and of the strongest discharge at the top.

Lines which are known to be due to fluorine, or are probably to be attributed to that element, are marked beneath the uppermost spectrum. Typical lines belonging to the four spectra of silicon are also indicated.

The photographs in Plates 1 and 2, and the first three on Plate 3, were taken with a large quartz spectrograph, Hilger's E 1.

Plate 1.—Region λ 7000 to λ 3400. The predominant lines in this region belong to Si I, Si II, and Si III.
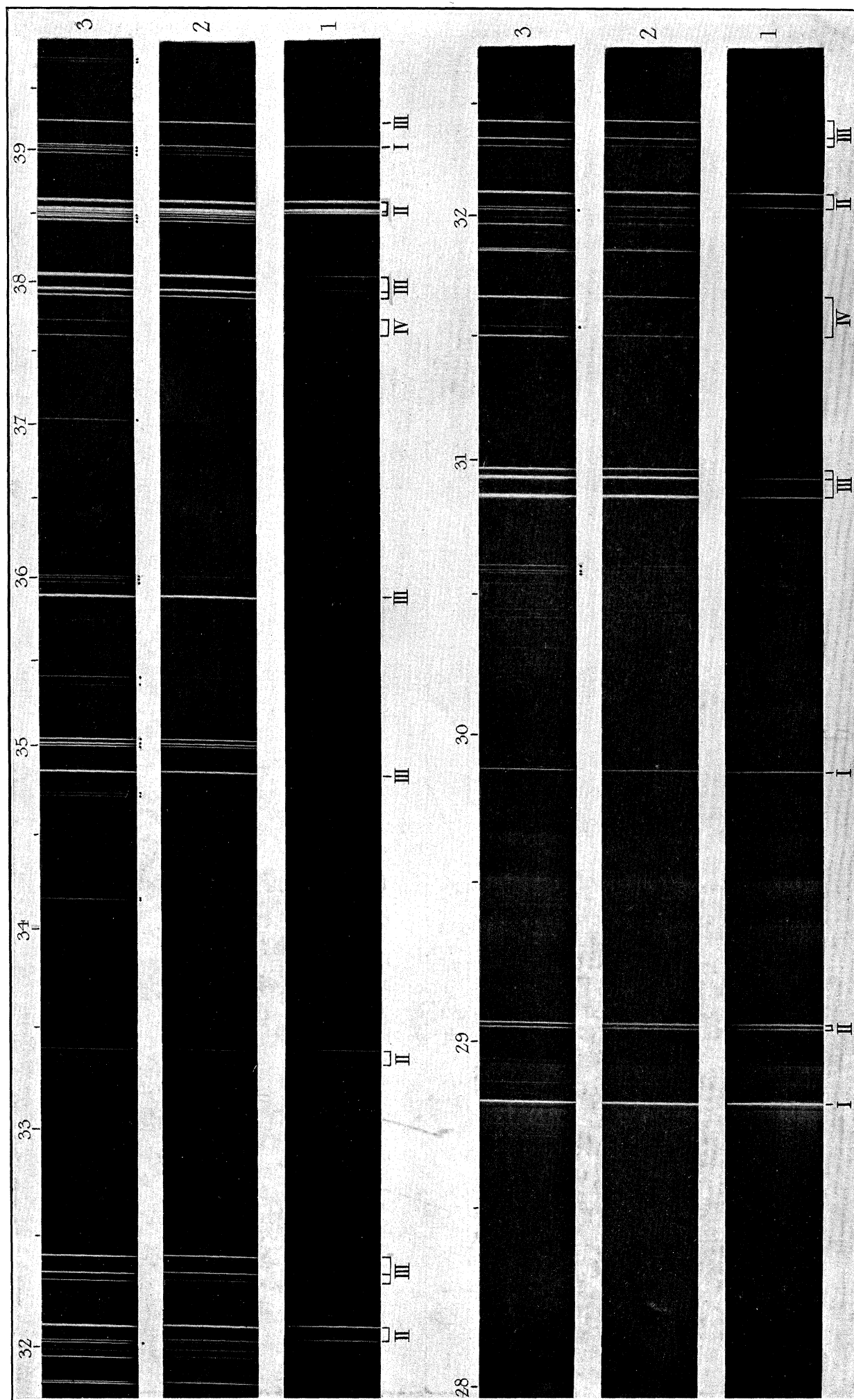
Plate 2.—Region λ 4000 to λ 2800.—The capillary tube was rather wider than that used for the spectra in Plate 1, and the lines are more sharply defined. A few faint lines of argon which appeared in No. 1 have been obliterated in the reproduction.

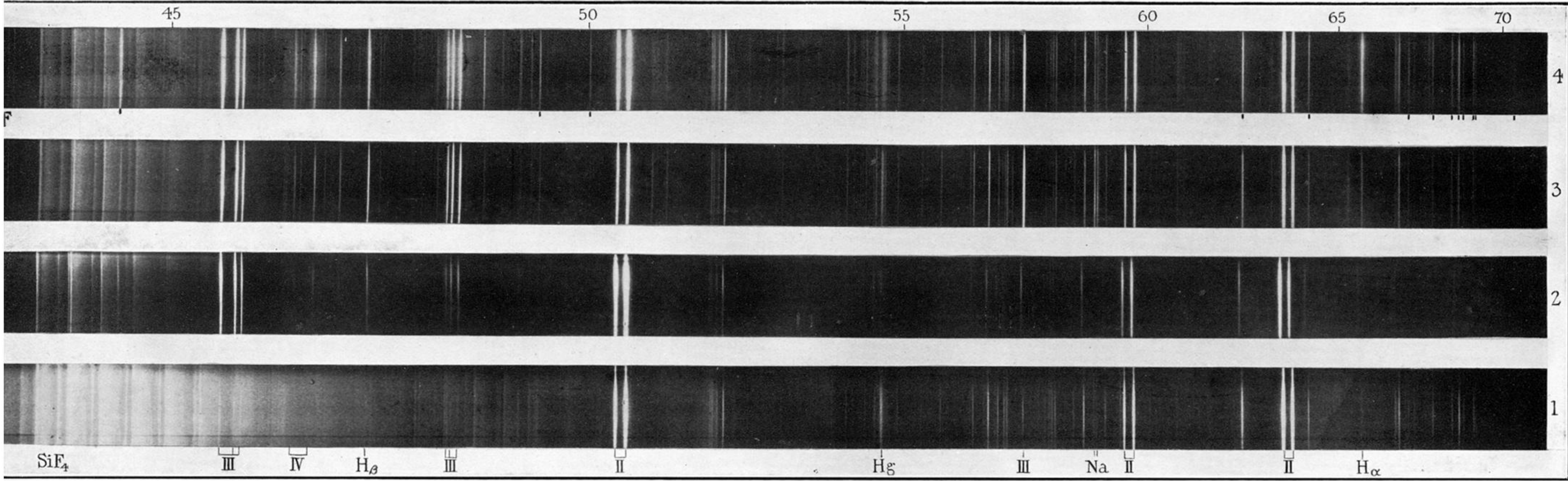*Plate* 3.—(1), (2), (3) : Vacuum tube spectra of Si F_4 in the region λ 2800 to λ 2400.

(4) : Arc spectrum of fused silicon in the region λ 2300 to λ 1840, with aluminium spark comparison. Taken with a small quartz spectrograph by BELLINGHAM and STANLEY.

(5), (6) : Spark spectrum of fused silicon in an atmosphere of hydrogen, region λ 1900 to λ 1250. A small amount of self-induction was introduced for No. 5, and it will be noted that the principal pair of Si IV, λλ 1393, 1402, is considerably reduced in intensity. Lines of aluminium and other impurities are present in these spectra.
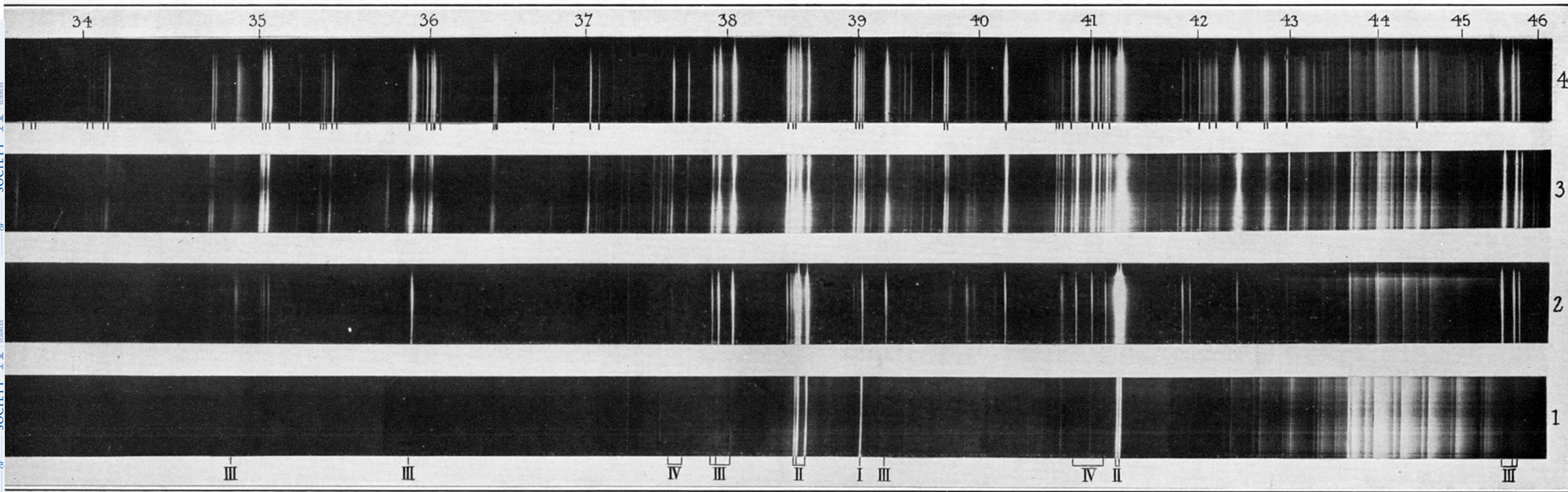
(7), (8) : Vacuum tube spectra of Si F_4 in the region λ 1900 to λ 1250. The discharge was strongest for No. 8, in which lines of Si III and Si IV are most strongly developed.
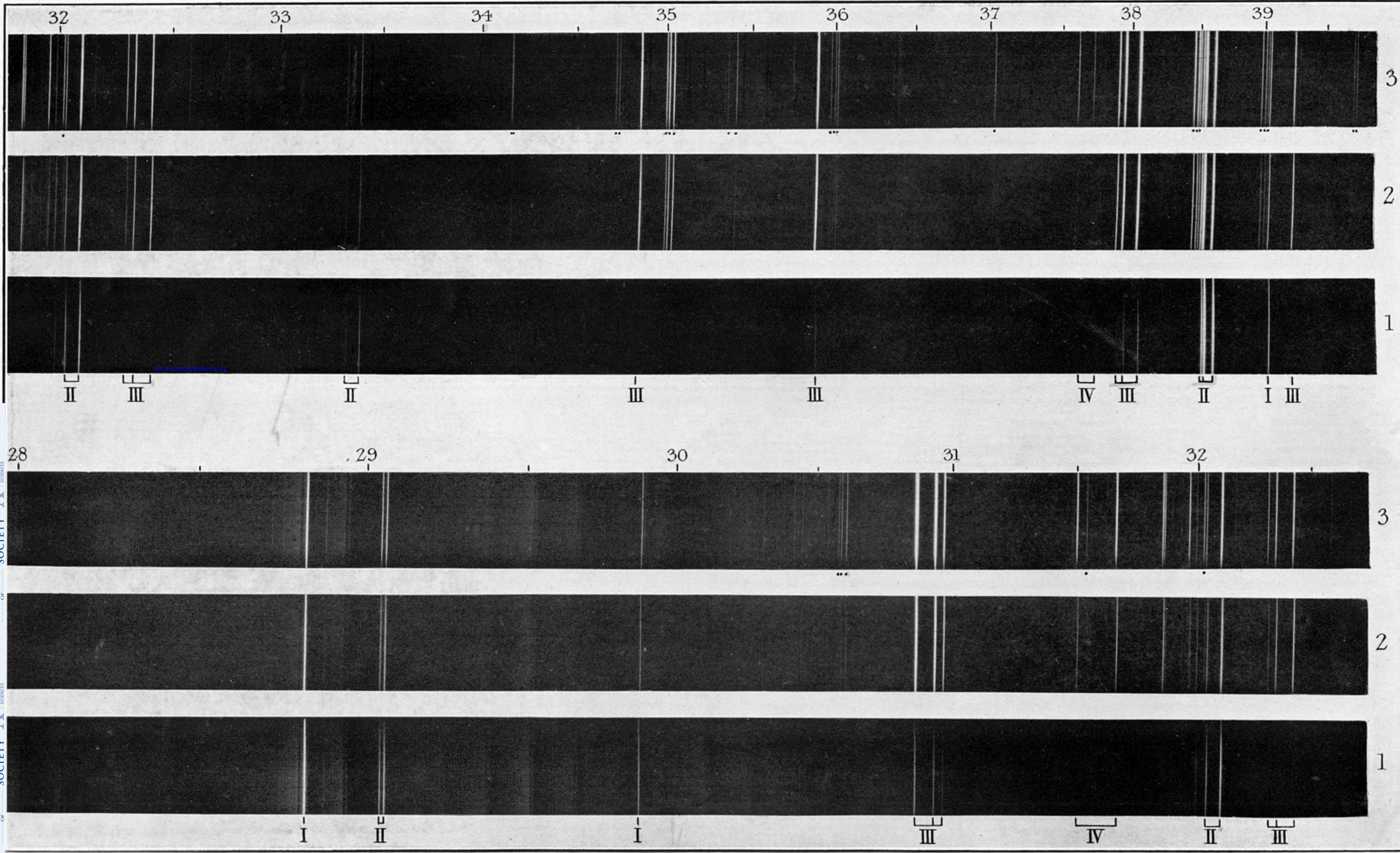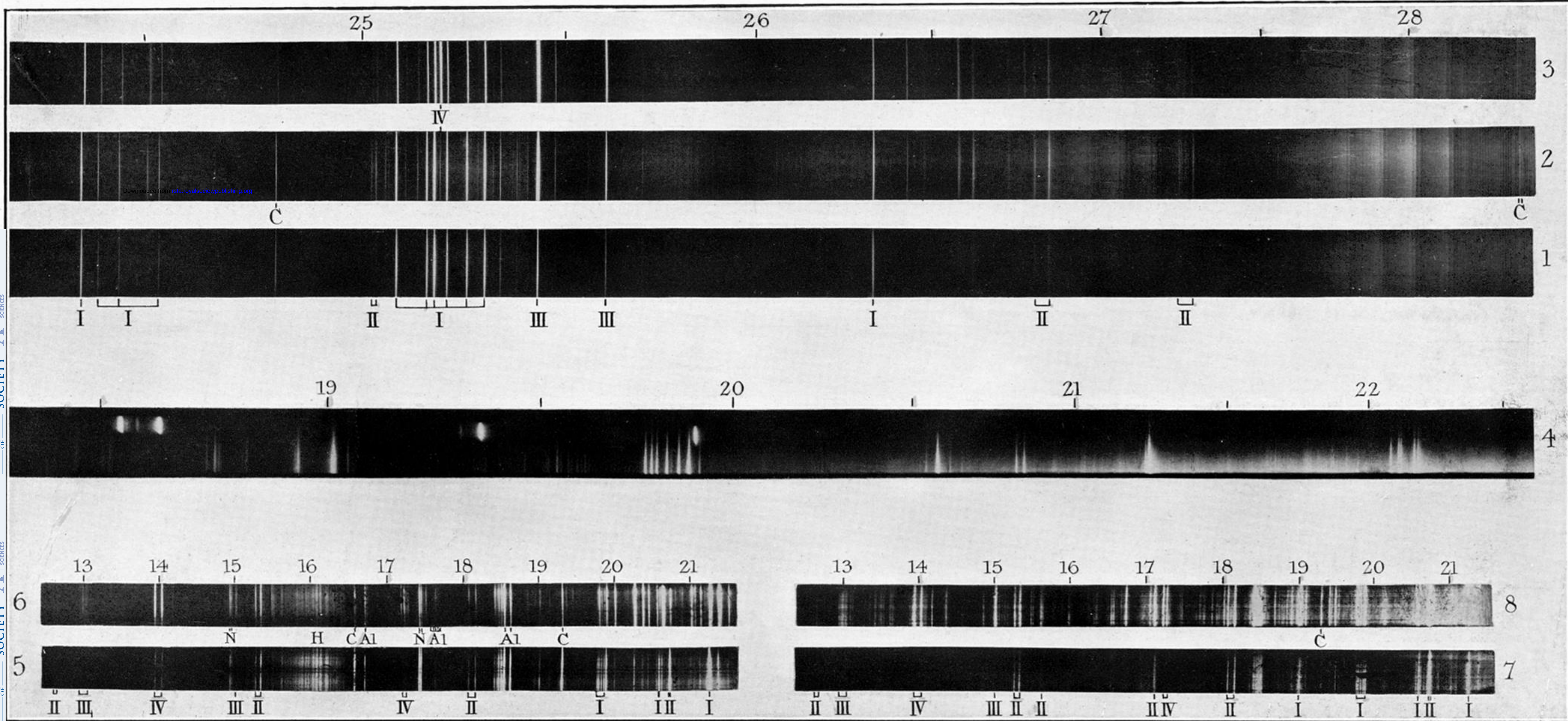
Progressive Spectra of Silicon (Si F$_4$ Vacuum tube).

Progressive Spectra of Silicon (Si F$_4$ Vacuum tube).

Spectra of Silicon : 3, 2, 1, 7, 8, Si F$_4$ Vacuum tube.   4, Arc.   5, 6, Spark in Hydrogen.

Progressive Spectra of Silicon (Si F₄ Vacuum tube).

Progressive Spectra of Silicon (Si F₄ Vacuum tube).

Spectra of Silicon : 3, 2, 1, 7, 8, Si F$_4$ Vacuum tube.   4, Arc.   5, 6, Spark in Hydrogen.