XXXII. The spectra of helium and hydrogen

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The black body gives a continuous spectrum. What would its brightness be when cut down to the narrow regions occupied by the D-lines? According to Abney's measures the brightness of that part of sunlight which lies between the D's would be about $\frac{1}{250}$ of the whole. We may perhaps estimate the region actually covered by the soda lines as $\frac{1}{25}$ of this. At this rate we should get

$$\frac{1}{25} \times \frac{1}{250} = \frac{1}{6250},$$

as the fraction of the whole radiation of the black body which has the wave-lengths of the soda lines. The actual brightness of a soda flame is thus of the same order of magnitude as that calculated for a black body when its spectrum is cut down to that of the flame, and we may infer that the light of a powerful soda flame is due much more to the widening of the spectrum lines than to an increased brightness of their central parts.

Terling Place, Witham,
Dec. 18.

XXXII. *The Spectra of Helium and Hydrogen.*

By E. J. EVANS, B.Sc., A.R.C.Sc.*

[Plate VI.]

INTRODUCTION.

THE investigation of the series spectra of hydrogen and helium has acquired considerable importance in consequence of recent theories on the structure of the atom, and the application of the quantum hypothesis to radiation problems.

It is known that some of the series spectra attributed to hydrogen can be represented with great accuracy by the Balmer-Rydberg-Ritz formula

$$\nu = K \left(\frac{1}{n_1^2} - \frac{1}{n_2^2} \right), \quad (1)$$

where ν represents the frequency, K Rydberg's universal constant, and n_1 and n_2 are whole numbers. If in equation (1) $n_1 = 2$, and n_2 takes the successive values 3, 4, 5, the ordinary hydrogen series in the visible spectrum is

* Communicated by Sir E. Rutherford, F.R.S.

obtained. The formula for this series was discovered by Balmer, and the series is usually referred to as the Balmer series. If $n_1=3$ a series of lines in the ultra-red is obtained, and two members of this series have been observed by Paschen. Also the series calculated by putting $n_1=1$ has been recently observed by Lyman * in the extreme ultra-violet. In addition to the lines represented by formula (1), some other series of lines have generally been ascribed to hydrogen. In 1896 Pickering † discovered in the spectrum of the star ξ Puppis a series of lines, which are closely represented by the formula

$$\nu = K \left\{ \frac{1}{2^2} - \frac{1}{(n + \frac{1}{2})^2} \right\} \cdot \cdot \cdot \cdot \cdot \quad (2)$$

On account of the numerical relationships existing between this series and the Balmer series, Pickering attributed the lines to hydrogen, and later Rydberg ‡, from analogy with the spectra of the alkali metals, considered the Balmer and Pickering series to be the diffuse and sharp series of hydrogen. He further concluded that the complete hydrogen spectrum should contain another series of lines, corresponding to the principal series in the spectra of the alkali metals, and given by the formula

$$\nu = K \left\{ \frac{1}{(1\frac{1}{2})^2} - \frac{1}{(n+1)^2} \right\} \cdot \cdot \cdot \cdot \cdot \quad (3)$$

Rydberg's conclusions were apparently strongly supported by the observation of a strong line in the spectra of certain stars and nebulae at the place calculated for the first line in formula (3).

A few years ago, Fowler § obtained the two series of lines represented by equations (2) and (3) by passing a condensed discharge from a 10-inch coil through mixtures of helium and hydrogen contained in an ordinary Plücker tube. Further, he observed in the spectrum of the mixed gases a third series related to the series represented by equation (3) in the same way as the Pickering series is related to the Balmer series, and which was approximately represented by the formula

$$\nu = K \left\{ \frac{1}{(1\frac{1}{2})^2} - \frac{1}{(n + \frac{1}{2})^2} \right\} \cdot \cdot \cdot \cdot \cdot \quad (4)$$

* Lyman, 'Nature,' xciii. p. 241.

† Pickering, *Astro-Phys. Journ.* vol. iv. p. 369 (1896); vol. v. p. 92 (1897).

‡ Rydberg, *Astro-Phys. Journ.* vol. vii. p. 233 (1899).

§ Fowler, *Monthly Notices R. A. S.*, Dec. 1912.

Fowler, in the absence of strict experimental proof, considered that Rydberg's theoretical investigations justified the conclusion that the three series of lines were due to hydrogen, and the series represented by (4) was called the second principal series of hydrogen. It is interesting to note that with the observation of series (4) the supposed analogy between the spectra of hydrogen and the alkali metals breaks down, as the spectra of the latter are known to have only one principal series.

Recently the problem of the origin of the series in question has been considered from the theoretical standpoint by Dr. Bohr*, who has arrived at very interesting results. Taking as basis Sir E. Rutherford's† atom-model, he has deduced with the aid of Planck's quantum hypothesis the following formula for the spectrum emitted by an atomic system consisting of a central positive nucleus and an electron moving round it :

$$\nu = \frac{2\pi^2 e^2 E^2 M m}{h^3 (M + m)} \left\{ \frac{1}{n_1^2} - \frac{1}{n_2^2} \right\}, \quad \dots \quad (5)$$

where e and m are the charge and mass of the electron, E and M the charge and mass of the nucleus, and h is Planck's constant. For a hydrogen atom according to Rutherford's theory, $E = -e$, and the formula can be written

$$\nu = \frac{2\pi^2 e^4 m}{h^3 \left(1 + \frac{m}{M}\right)} \left\{ \frac{1}{n_1^2} - \frac{1}{n_2^2} \right\} \dots \dots \quad (6)$$

where the bracket multiplying h^3 is very nearly equal to unity on account of the great mass of the nucleus compared with that of the electron. It was shown by Bohr that the above expression, on putting in the values of the constants, agreed within the limits of experimental error with formula (1).

It will be seen that formula (6) does not include the lines observed by Pickering and Fowler, and given by formulæ (2), (3), and (4). However, if in equation (5) $E = -2e$, which according to Rutherford represents the helium atom, the following formula is obtained for the frequency of the lines :

$$\nu = \frac{2\pi^2 e^4 m}{h^3 \left(1 + \frac{m}{M}\right)} \left\{ \frac{1}{\left(\frac{n_1}{2}\right)^2} - \frac{1}{\left(\frac{n_2}{2}\right)^2} \right\} \dots \dots \quad (7)$$

* N. Bohr, Phil. Mag. xxvi. pp. 1, 476, 857 (1913); xxvii. p. 506 (1914).

† Sir E. Rutherford, Phil. Mag. xxi. p. 669 (1911).

As the factor outside the bracket differs from that in formula (6) only by a small correction due to the difference in the masses of the hydrogen and helium nuclei, it will be seen that equation (7) approximately represents the series of lines given by (2), (3), and (4). Bohr therefore suggested that the lines in question were not due to hydrogen but to helium. This conclusion was not disproved by previous observations and experiments, for helium was always known to be present when the lines appeared. Bohr also pointed out that the reason why the lines considered are not observed in ordinary helium tubes may be that in such tubes the ionization of the gas is not as complete as in the star ξ Puppis or in Fowler's experiments with the condensed discharge. According to the theory, the presence of helium atoms which have lost both electrons is necessary for the appearance of these lines in a spectrum-tube.

Preliminary experiments by the author* gave strong support to Bohr's conclusions. A helium spectrum was obtained showing the first line (λ 4686) of the series represented by equation (3) very brightly, but no trace of the ordinary hydrogen lines of the Balmer series. Also this line could not be observed in the spectrum obtained by passing a strong discharge through mixtures of hydrogen and neon, and of hydrogen and argon. Later Stark† observed the 4686 line in a helium tube in which the hydrogen lines did not appear. Further evidence pointing to the same conclusion has been given by Rau‡, who has made some interesting experiments on the voltage necessary for the production of spectrum lines.

In a discussion in 'Nature,' Fowler§ pointed out that the lines observed by him were not accurately represented by formulæ (2), (3), and (4), but Bohr|| subsequently showed that the deviations from the values given by the formulæ could be accounted for within the limits of experimental error by taking into account the correction due to the mass of the central nucleus. This influence of the mass of the nucleus was not considered in Bohr's original paper. Recently Fowler¶ has published a very important paper on series lines in spark spectra. He concludes from analogy with spark spectra of the enhanced type, that the lines represented by equations (2), (3), and (4) are enhanced lines

* Evans, 'Nature,' xcii. p. 5.

† Stark, *Verh. d. Deutsch. Phys. Ges.* xvi. p. 468 (1914).

‡ Rau, *Sitzungsb. d. Phys.-Med. Ges. Würzburg*, 1914.

§ Fowler, 'Nature,' xcii. p. 95. || Bohr, 'Nature,' xcii. p. 231.

¶ Fowler, *Phil. Trans. A.* vol. ccxiv. p. 225.

of helium. Stark also came to the same conclusion with respect to the line 4686.

In the above mentioned discussion in 'Nature' Bohr showed that if his view was correct, the helium spectrum should contain another series of lines, which are represented by the formula

$$\nu = K' \left\{ \frac{1}{(2)^2} - \frac{1}{(n)^2} \right\} \quad . \quad . \quad . \quad . \quad . \quad (8)$$

where K' is the constant outside the bracket in formula (7). This formula is obtained from (7) by putting $n_1=4$ and $n_2=6, 8, 10 \dots$. The lines of this series should appear near the hydrogen lines of the Balmer series, and their wave-lengths were calculated to be 6560.4, 4859.5, 4338.9, 4100.2. These lines and the Pickering lines can be represented by one formula

$$\nu = K' \left\{ \frac{1}{(2)^2} - \frac{1}{\left(\frac{n}{2}\right)^2} \right\} \quad . \quad . \quad . \quad . \quad . \quad (9)$$

and the intensity of all the lines should decrease regularly with increasing values of n . The lines would be difficult to detect, especially if hydrogen was present in any quantity, as it is known from Fowler's experiments that the Pickering lines are faint even when photographed with instruments of small dispersion. The presence of the lines given by formula (8) would greatly strengthen the experimental evidence in favour of Bohr's theory, but their absence would immediately show that the theory was incorrect. The investigation of the lines in question, and the determination of more accurate values for the wave-lengths of the lines of the Pickering series, formed the main object of the present research.

THE EXPERIMENTAL ARRANGEMENT.

The method which was chiefly employed for the production of the spectrum lines was very similar to that previously described by Fowler. A 20-inch coil with a condenser across its terminals was connected to a helium spectrum-tube in series with which was placed an adjustable spark-gap. The spectrum produced was examined visually with a Hilger direct-reading instrument, and the wave-lengths could be read off with an accuracy of 1 or 2 A.U. For the purpose of photographing the lines, four different instruments were employed. In the first series of experiments the lines were photographed by means of a small quartz spectrograph giving

a dispersion of 250 A.U. per mm. in the red, 130 A.U. per mm. in the green, and 76 A.U. per mm. in the violet. Later the spectrum was photographed with a concave grating of 1 metre radius ruled with 14,000 lines to the inch. By means of this instrument it was found possible to obtain the first members of series (3) and (4), but no trace of any of the lines represented by equations (2) and (8) even after exposures of 40 hours. A few members of the series represented by equation (2) were obtained in the first place by employing a spectroscope consisting of two glass prisms, which gave a dispersion of 150 A.U. per mm. in the red, 54 A.U. per mm. in the green, and 30 A.U. per mm. in the violet. Finally these two prisms were replaced by others giving greater dispersion and capable of resolving 2 A.U. at λ 6500. For the sake of comparison the dispersions given by this prism spectroscope in the red, green, and violet were 75, 27, and 15 A.U. per mm. respectively. The time of exposure varied from 20 minutes to 30 hours, depending upon the dispersion of the apparatus and the particular lines studied. The first member of series (3) at 4686 was easily photographed, but the series represented by formula (9) required a very long exposure, and even then only a few members of the series could be detected with certainty. All the photographs were taken with Wratten and Wainwright's panchromatic plates and films.

The spectrum-tubes employed were of various shapes and dimensions. The diameter of the capillary was varied from .8 to 3.5 mm., and its length from 3 to 8 cm. When the lines represented by equation (9) were studied, a spectrum-tube with a capillary of .8 mm. was chosen, the spark-gap was made 1.2 cm., and the pressure of the helium was adjusted to about .5 mm. of mercury. Photographs of the 4686 line were taken with spectrum-tubes having capillaries of different bore, and containing helium at pressures ranging from .36 to 2 mm.

Since the hydrogen lines of the Balmer series are in ordinary circumstances much stronger than the odd members of series (9), it was necessary, especially with the relatively small dispersion employed, to obtain a helium spectrum giving little or no trace of the hydrogen lines. In the preliminary experiments spectrum-tubes with aluminium electrodes were employed, but it was found impossible to remove the hydrogen from the electrodes in a reasonable time. Later, thin platinum electrodes of .4 mm. diameter were employed, and a helium spectrum showing no trace of hydrogen was obtained. In this connexion it is interesting

to note that it is comparatively easy to obtain a helium spectrum showing no trace of the hydrogen lines of the Balmer series if an ordinary discharge is sent through a spectrum tube containing purified helium. With the condenser discharge, however, the hydrogen lines usually appear in the bulbs, although they are often not present in the capillary. This was also observed by Curtis* during a research on the band spectrum of helium.

The arrangement of the apparatus and the method of conducting the experiments are made clear by reference to the accompanying diagram.

In the diagram, E represents the spectrum tube and A, C, F, and G bulbs containing carefully prepared coconut charcoal. The tap B was placed at a distance of 1 metre from the spectrum-tube, and the discharge scarcely ever reached it. A Töpler pump and a tube of P_2O_5 were attached to H, and the whole apparatus was evacuated to a pressure of 1/100th of a mm. of mercury. The charcoal bulbs C, F, and G were then heated for several hours until no more gas was given off. Also the bulbs and the capillary of the spectrum-tube were heated until the softening point of glass was reached. The gases given off during the heating process were absorbed by the charcoal bulb A, which was immersed in liquid air. The tap B was then closed and the gas absorbed by the charcoal in A removed by heating. The bulb A was again immersed in liquid air, and the helium containing a small quantity of impurities was then introduced through the side-tube K and allowed to remain in that part of the apparatus for over an hour. The charcoal bulbs C, F, and G were now immersed in liquid air, and the tap B was opened so that helium could enter the spectrum-tube. The pressure of the gas was then adjusted to 3 mm. by means of the pump and McLeod gauge, and the ordinary discharge (without condenser) passed through the tube. The current

* Curtis, Proc. Roy. Soc. A. vol. lxxxix. p. 146 (1913).

passing through the primary of the induction-coil was adjusted until the cathode was almost white-hot, and it was kept at this temperature for nearly four hours. By reversing the direction of the current passing through the tube, the other electrode was treated in a similar manner. This process was repeated until no hydrogen lines were visible in the Hilger direct-reading spectroscope. The condenser discharge was then passed through the tube for 30 minutes, and both the bulbs and capillary were examined for the presence of the hydrogen lines. If the lines eventually appeared, the process of heating the electrodes was continued until the spectrum showed no hydrogen lines after the passage of a heavy condenser discharge for one hour. During these experiments the platinum electrodes spluttered to the sides of the spectrum-tube and consequently became much finer. This was also made evident by the bending of the electrodes to touch the sides of the bulbs when a heavy condenser discharge was passed through the tube. In later experiments, the diameters of the bulbs were so adjusted that the platinum electrodes would not touch the sides even when perpendicular to their original directions. In the preliminary experiments, all the photographs and observations were obtained with the spectrum-tube in the vertical position, but later, especially when investigating the series represented by equation (9), the tube was usually placed in the end-on position with the capillary pointing towards the spectroscope.

The spectrum obtained by passing the ordinary discharge without condenser and spark-gap through a tube containing helium at a pressure of .25 mm. was also studied. Under these conditions a stream of charged particles, which were deflected by a magnet in the same direction as cathode rays, passed down the tube. The results of experiments carried out in this way will be described later.

For the determination of wave-lengths, the lines of the ordinary helium spectrum were employed as standards except in the red and yellow, where they are too far apart. In these regions, the impurity lines of mercury, sodium, silicon, and oxygen were found useful. Also in some cases the wave-lengths were determined with the aid of a copper or barium comparison spectrum. The mercury lines only appeared on one of the plates, but the sodium, silicon, and oxygen lines were always present on photographs taken when a heavy condenser discharge was passed through the tube. These lines are due to the decomposition of the glass of the capillary by the discharge.

EXPERIMENTAL RESULTS.

The Series given by Formulae (3) and (4).

The preliminary experiments * showed that it was possible to obtain photographs showing the 4686 line very strongly, and no trace of the ordinary hydrogen lines of the Balmer series. As the photographs were taken with a quartz spectrograph of small dispersion, the wave-length could only be determined with an accuracy of about 1 A.U. The line was therefore photographed with the prism spectroscope giving the greatest dispersion, and the wave-length determined with a greater degree of accuracy. The mean wave-length as determined from these photographs was $4686\cdot00 (\pm 0\cdot05)$, which agreed well with the value $4685\cdot98 (\pm 0\cdot01)$ determined by Fowler from a photograph taken with a 10-foot concave grating.

It was also possible to obtain this line, employing the same spectroscope, by passing the ordinary discharge without condenser and spark-gap through an end-on tube containing helium at a pressure of $\cdot 25$ mm. The line is shown in photograph I. (Pl. VI.), where it appears fairly strong and broad in the capillary. The wave-length of the line was measured and found to be $4685\cdot94$. The photograph does not show the presence of the hydrogen lines at 6563, 4861, but only the ordinary helium lines and the 4686 line.

These experiments show that it is possible to obtain the first member of series (3) from a helium tube giving no trace of the hydrogen lines of the Balmer series.

The Series given by Formula (9).(A) *Experiments with tubes containing aluminium electrodes.*

The second member of this series was observed visually for the first time in the spectrum of an end-on tube with a narrow capillary. Two members of the series are shown in photograph II., which was taken with the two-prism spectroscope of low dispersion. The wave-lengths of these lines were determined with an accuracy of $0\cdot2$ A.U., and were found to agree within the limits of experimental error with the values calculated for the second and fourth members of series (9). The two values obtained were $5411\cdot63$ and $4541\cdot93$ respectively. The wave-lengths of the lines as determined by Fowler were $5410\cdot5 (\pm 1\cdot0)$ and $4541\cdot3 (\pm 0\cdot25)$. In addition to the ordinary helium lines, shorter or capillary

* Evans, *loc. cit.*

lines due to oxygen, silicon, and sulphur made their appearance in the spectrum. The photograph also shows the presence of the H_α (6563), H_β (4861) . . . lines of hydrogen and the mercury line at 5460. These lines stretch across the capillary and have the same length as the ordinary helium lines. The 5411 and the 4542 lines also pass through the capillary spectrum, but their lengths are only about one half that of the ordinary helium lines. The line at 5411 was also found to be more intense and sharper than the 4542 line. The sixth member of series (9) could not be detected on the photographic plate. A thorough examination of the plate near the H_α and H_β lines did not reveal the presence of any faint lines at 6560.4 and 4859.5. Rough measurements, however, showed that the widths of the H_α and H_β lines were approximately 8.1 and 5 A.U. respectively. Also the line at 5411 was found to be narrow compared with the hydrogen lines. Since the even members of series (9) were so faint compared with the hydrogen lines, it was decided to repeat the experiments with a prism spectroscope of nearly double the dispersion and tubes provided with thin platinum electrodes.

(B) *Experiments with spectrum tubes provided with platinum electrodes.*

A condenser discharge was sent through an end-on tube containing helium at a pressure of .4 mm., and three photographs were taken with the two-prism spectroscope of greatest dispersion after exposures of 5, 12, and 26 hours respectively. In the last case the direction of the discharge was reversed at the end of 13 hours. On all the plates a faint line appeared at 6560, which is the calculated position for the first line of series (9). This line was shorter than the ordinary helium lines, and the oxygen lines at 6455 and 6157, but longer than the silicon capillary lines at 6371 and 6347.

The plates taken with exposures of 12 and 26 hours showed in addition to the 6560 line an ill-defined capillary line at 6564. The nature of the line made accurate measurements impossible, and the origin of the line is unknown unless it is due to a trace of hydrogen. On the same plate there also appeared a line at 5411, which was of the same general character as the 6560 line but of less intensity. The third member of the series at 4859.5 could not be detected on the plates taken with exposures of 5 and 12 hours, and the only lines present in this region were the oxygen capillary lines at 4872, 4865, 4861, and 4857. The plate taken with an

exposure of 26 hours was also examined in the same region, and the wave-lengths of two very faint lines, which extended beyond the capillary, were measured. One of these lines, which had a wave-length of 4861.7 A.U., was longer than the 6560 line. The other line was fainter than the 4861 line, and its measured wave-length was 4859.5. The fourth member of the series which should appear at 4542 could not be detected on any of the plates. All the lines between 7065 and 4713 on the plate taken with an exposure of 12 hours were measured, and with the exception of capillary lines at 6721.5, 6641.1, 5739.3, 4829.3, 4813.7, all the others could be attributed to helium, oxygen, silicon, sodium, and chlorine. These experiments show that when a condenser discharge was passed through helium, two lines were obtained whose wave-lengths agreed within the limits of experimental error with the values calculated for the first and second members of series (9), and whose intensities fell off with diminishing wave-length. Also a very faint line was obtained whose wave-length was very approximately the same as that calculated for the third member of the series represented by equation (9). However, in view of the faintness of the line and the appearance of another stronger line of unknown origin close to it, the question whether the line is the third member of the series cannot be regarded as settled.

The experiments described above show that very long exposures are required to bring out the lines of the series given by equation (9), for even with exposures of 26 hours only two lines could be detected with certainty. It was therefore considered desirable to obtain photographs with the other prism spectroscope, which gave a lower dispersion. Two photographs were taken, one with an exposure of 21 hours (photograph III.), and the other with an exposure of 31 hours. In the latter case, the discharge was reversed in direction at the end of half the exposure. The wave-lengths of the first two lines were measured for each plate, and found to be 6560.69, 5411.95, and 6560.10, 5411.71 respectively. A third line at 4860.5 was also obtained, but its wave-length was 1 A.U. greater than the value calculated theoretically for the third member of the series. Also, the line had too great an intensity if it was to be regarded as the third member of the series in which 6560 and 5411 were the first and second members respectively. It is interesting to point out that the wave-length (4860.5) is approximately the mean of the two values 4861.7 and 4859.5 obtained for the two faint lines photographed with the spectroscope of greater dispersion. The appearance of the line also suggested

that it might possibly be a double line. A faint fourth line of the right order of intensity in the blue region of the spectrum was also measured, and its wave-length (4542.2) is found to agree within the limits of experimental error with the calculated value (4541.80) for the fourth member of the series.

When the above exposures were concluded, the helium was pumped out of the spectrum-tube and replaced by oxygen. A condenser discharge was then sent through the tube for 4 hours, and a photograph taken. The lines on this plate between 6800 and 6157 were measured, and no evidence was found of the presence of a line at 6560. A line at 6563.5, probably due to hydrogen, was however obtained. The two lines at 6721 and 6641, and impurity lines due to nitrogen and silicon, were also present.

EXPERIMENTS WITH THE ORDINARY DISCHARGE.

In these experiments, the ordinary discharge was passed through an end-on tube containing helium at a pressure of .25 mm. The same spectroscope was employed as in the experiments described in the last section, but the slit was widened in consequence of the comparatively small intensity of the light. The exposure was varied from 9 to 12 hours and a copper comparison spectrum was sometimes utilized for the determination of wave-lengths. The discharge was also reversed in direction when half the time of exposure had elapsed. A series of lines with wave-lengths approximately the same as those calculated from equation (9) appeared in the capillary in addition to the 4686 line. The wave-length measurements in this case were not as accurate as before, because of the greater breadth of the lines. The mean values of the wave-lengths obtained for the first four lines are 6560.71, 5411.44, 4860.5, 4542.44. For one of the photographs the measurements were extended still further towards the violet, and lines which are possible members of series (9) were obtained at 4339.97 and 4199.9. All the lines on this photograph (photograph IV.) between 6678 and 3819 were measured, and with the exception of the above lines and two others at 4358.7 and 4226.9, they were all due to helium and oxygen. In all the photographs taken with the ordinary discharge the third line at 4860.5 was stronger than it should be if it was the third member of series (9).

The accompanying table gives the wave-lengths of the lines which have been determined from photographs taken

with the condenser discharge and also the ordinary discharge, together with the values calculated from Bohr's theory. The values given for the first four lines were determined from photographic plates taken with the condenser discharge, whilst the last two values were deduced from photographs taken with the ordinary discharge. The dispersion in the particular region of the spectrum and the probable error are also included in the table.

Wave-length calculated.	Wave-length observed.	Limit of error.	Dispersion.
6560.38	6560.43	0.5	75 AU per mm.
5411.74	5411.67	0.2	45 AU per mm.
4859.54	?		
4541.80	4541.93	0.2	35 AU per mm.
4338.88	*4339.97	0.4	36 AU per mm.
4200.03	4199.95	0.4	30 AU per mm.

* Two or three oxygen lines in the neighbourhood of this line may affect the observed value.

SUMMARY.

The experiments have shown :—

(A) That it is possible to observe the first member (4686) of the series

$$\nu = 109750 \left\{ \frac{1}{\left(1\frac{1}{2}\right)^2} - \frac{1}{\left(\frac{n}{2}\right)^2} \right\},$$

which includes the lines given by formulæ (3) and (4), and also a line which agrees in wave-length with the first member (6560.4) of the series

$$\nu = 109750 \left\{ \frac{1}{(2)^2} - \frac{1}{\left(\frac{n}{2}\right)^2} \right\},$$

which includes the Pickering lines and the lines at 6560.4... predicted by Bohr, in a helium tube giving no trace of the hydrogen lines.

(B) That the experimental values for the wave-lengths of the Pickering lines agree with the theoretical values calculated by Bohr within the limits of experimental error.

These results strongly point to the conclusion that the

series spectrum of hydrogen consists only of lines which are represented by the formula

$$\nu = 109704 \left(\frac{1}{n_1^2} - \frac{1}{n_2^2} \right),$$

and that the series spectrum of helium in addition to the ordinary helium lines consists of all the lines which are represented by the formula

$$\nu = 109750 \left\{ \frac{1}{\left(\frac{n_1}{2}\right)^2} - \frac{1}{\left(\frac{n_2}{2}\right)^2} \right\}.$$

The author wishes to thank Sir Ernest Rutherford for bringing the subject of the present investigation to his notice and for valuable suggestions and encouragement during the course of the research.

The University of Manchester,
Dec. 1914.

XXXIII. *Simplified Deduction of the Formula from the Theory of Combinations which Planck uses as the Basis of his Radiation Theory.* By P. EHRENFEST and H. KAMERLINGH ONNES*.

WE refer to the expression

$$C_P^N = \frac{(N-1+P)!}{P!(N-1)!}, \quad \dots \quad (A)$$

which gives the number of ways in which N monochromatic resonators $R_1, R_2, \dots R_N$ may be distributed over the various degrees of energy, determined by the series of multiples $0, \epsilon, 2\epsilon \dots$ of the unit energy ϵ , when the resonators together must each time contain the given multiple $P\epsilon$. Two methods of distribution will be called identical, and only then, when the first resonator in the one distribution is at the same grade of energy as the same resonator in the second, and similarly the second, third, $\dots$ and the N th resonator are each at the same energy-grades in the two distributions.

Taking a special example, we shall introduce a symbol for the distribution. Let $N=4$, and $P=7$. One of the possible distributions is the following: resonator R_1 has reached the

* Communicated by the Authors.

I.

II.

III.

IV.