THE BALMER SERIES OF HYDROGEN, AND THE QUANTUM THEORY OF LINE SPECTRA.

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SYNOPSIS.

Balmer Series of Hydrogen.—(1) *A rigid comparison of experimental with theoretical results* is the main purpose of the paper. It is concluded that Merton's measurements of the separation, half-width and relative intensity of the H_α and H_β doublets check with values derived from the recent Bohr-Kramers developments of the quantum theory, if a general field of 100 volts per cm. is assumed. After the fine structure has been analyzed and the "circle" line computed, determining the position of the components from the Sommerfeld theory and the relative intensities from the Bohr-Kramers theory, the frequencies of all lines are fitted into the Bohr relativity formula. (2) *The Rydberg constant* for H is then calculated to be 109,677.7 ± 0.2. (3) *A discussion of observations in mixtures of hydrogen and helium* made by Merton and Nicholson at relatively high pressures concludes the paper.

Rydberg spectral series constant for a nucleus of infinite mass is computed to be 109,736,9 ± 0.2.

INTRODUCTION.

THE purpose of this paper is to make as accurate a comparison as possible between the best experimental results for the Balmer series of hydrogen, and the theoretical results to be expected according to the latest developments of the quantum theory of line spectra. The experimental data are as follows:

1. Grating measurements by Paschen[1] of H_α, H_β, H_γ, and H_δ, (all unresolved) giving 6562.797, 4861.326, 4340.465, and 4101.735 I.A. respectively. The experimental error is estimated at ±0.004 Å. in each case.

2. Grating measurements by Paschen[1] of H_α (resolved) giving 6562.853 and 6562.732 I.A. for the components.

3. Interferometer measurements by Meissner[1] of H_α, giving a doublet, 6562.849 and 6562.725 I.A., of intensity 7 and 5 respectively, and of H_β (unresolved) giving 4861.329 I.A.

4. Grating measurements by Curtis[2] of the first six lines of the series (all unresolved) giving 6562.793, 4861.326, 4340.467, 4101.738, 3970.075, and 3889.051 I.A. respectively. The probable errors range from 0.0017 Å. to 0.0006 Å. (see Table II., column 3). The correct reduction to vacuum

[1] Ann. d. Phys. (4), 50, 901, 1916.

[2] Proc. Roy. Soc., A, 90, 605, 1914.

and a discussion of various possible series formulae was given by Curtis[1] in 1919.

5. A study by Merton[2] of the fine structure of H_α and H_β, under various experimental conditions. These results supplement and in part correct previous results by Merton and Nicholson.[3] The later results are to the effect that the most distinct doubling of both H_α and H_β is observed at liquid air temperature, in a mixture of helium and hydrogen at a few millimeters pressure. Under these conditions H_α is a doublet of 0.1446 Å. separation, the components having a half-width of 0.028 Å. and an intensity ratio of 2.18 to 1 (the red component being the stronger). H_β is a doublet of 0.093 Å. separation, and 0.045 Å. half-width of components. The intensity ratio was not measured. Further details of this work are given later in the present paper.

6. Data by Merton and Nicholson[4] and by Wood[5] as to the appearance of higher members of the Balmer series in mixtures of hydrogen and helium, at relatively high pressures, and in long vacuum tubes respectively.

There are also data on the Stark effect for the Balmer series, but this subject will not be discussed, since the agreement between theory and experiment, in the case of strong electric fields, has already been shown by Kramers[6] to be perfect. The results for weak fields will however be treated, in connection with the fine structure of the lines.

The quantum theory of line spectra, as applied to the Balmer series, may be summarized as follows:

In 1914–1915 Bohr[7] applied Rutherford's nuclear theory of the atom and general quantum theory to the case particularly of a single electron of charge e and mass m revolving about a nucleus of charge Ne and mass M. On the hypothesis of circular orbits, and the atomicity of angular momentum, the Balmer formula

$$\nu = \nu_1 = N_0 N^2 \left(\frac{1}{n''^2} - \frac{1}{n'^2} \right) \qquad (1)$$

was theoretically deduced. In this expression the angular momentum in the initial state of the electron is given by $n'h/2\pi$, in the final state by $n''h/2\pi$. For the Balmer series $n'' = 2$, $n' = 3, 4, 5$ etc. $N = 1$ for all Hydrogen series and $N = 2$ for Helium enhanced series. N_0 is the

[1] Proc. Roy. Soc., A, 96, 147, 1919.
[2] Proc. Roy. Soc., A, 97, 307, 1920.
[3] Phil. Trans., A, 217, 237, 1917.
[4] Proc. Roy. Soc., A, 96, 112, 1919.
[5] Proc. Roy. Soc., A, 97, 455, 1920.
[6] D. Kgl. Danske Vid. Selsk. Skr. natur og math. Afd., 8, R. III., 3, 1919.
[7] Phil. Mag., 26, 1, 476, and 857, 1913; 27, 507, 1914; 29, 332, 1915; 30, 394, 1915.

so-called Rydberg constant, and is *not* a constant, depending for its value on the mass of the nucleus. For Hydrogen it is designated N_ω and is given theoretically by $N_\infty \times M_H/(M_H + m)$, where N_∞ is the constant for a nucleus of infinite mass and given by $2\pi^2 e^4 m/ch^3$, in terms of frequency number. The spectroscopically observed value of N_ω and the theoretical value deduced from this expression check within the limits of experimental error.[1] Because however of the relatively large errors in "h" and "e," and the small error in N_ω (regardless of the particular formula used for the Balmer series), N_ω must be considered as an undetermined constant, in testing various series formulæ.

In 1915 Bohr[2] applied relativity mechanics to his atomic model, and thus obtained, in place of (1), the more complex expression

$$\nu = \nu_1 + \nu_2 = \nu_1 + 1/4 N_0 \alpha^2 N^4 \left(\frac{1}{n''^4} - \frac{1}{n'^4} \right), \tag{2}$$

where $\alpha = 2\pi e^2/hc$. Equation (2) is frequently written

$$\nu = N_0 N^2 \left(\frac{1}{n''^2} - \frac{1}{n'^2} \right) \left[1 + \frac{\alpha^2 N^2}{4} \left(\frac{1}{n''^2} + \frac{1}{n'^2} \right) \right]. \tag{2'}$$

Equation (2) or (2') indicates a shift of all wave-lengths to the violet as compared with the values given by equation (1). For the Balmer series this shift varies from 0.039 Å. for H_α to 0.010 Å. for the head of the series. Since the frequencies given by (2) correspond to an electron falling from one circle to another circle, the corresponding spectral lines will be called "circle lines."

In 1915–1916 Sommerfeld[3] extended the Bohr theory to the case of elliptic orbits. For a "hydrogen-like" atom, *i.e.*, a single electron revolving about a nucleus, there is both angular and radial momentum. The angular momentum is constant and is given by $n_2 h/2\pi$. The radial momentum has an average value of $n_1 h/2\pi$. The total momentum is given by $nh/2\pi$ where $n = n_1 + n_2$, and as before n' will be used to designate the initial state and n'' the final. The emitted frequency is then given by

$$\nu = \nu_1 + \nu_2 + \nu_3, \tag{3}$$

where

$$\nu_3 = N_0 \alpha^2 N^4 \left[\frac{1}{n''^4} \left(\frac{n_1''}{n_2''} \right) - \frac{1}{n'^4} \left(\frac{n_1'}{n_2'} \right) \right]. \tag{4}$$

Equation (3) indicates the so-called "fine-structure" of spectral lines. Each line given by the Bohr theory (*i.e.*, each circle line) is split up into

[1] Birge, PHYS. REV., 14, 363, 1919.

[2] Phil. Mag., 29, 332, 1915.

[3] Main article, Ann. d. Phys., 51, 1–125, 1916.

a number of components, obtained by combining the various possible states $n_1'' + n_2'' = n'' =$ constant, with the possible states $n_1' + n_2' = n$ = another constant. This is now known as the "combination-principle." Formulæ (2) and (3) are both approximate, terms in $(\alpha N)^4$ and higher powers having been neglected in comparison with $(\alpha N)^2$. It is only in the case of X-ray spectra that these higher powers need be considered. (See Sommerfeld, loc. cit., p. 55.)

In discussing the relative intensity which the various fine structure components of a line might be expected to possess, Sommerfeld made certain arbitrary assumptions, as his theory gave no theoretical basis for the matter. Paschen (loc. cit.) tested these assumptions, using the "4686" helium enhanced series, in which the "fine structure" is sixteen times as broad as in the corresponding hydrogen series, due to the N^4 term in (4). Paschen concluded that the fine structure components agreed in position with Sommerfeld's theory, but agreed only partially in intensity, especially in the case of the spark discharge. Paschen found a striking difference in appearance between the spark and the constant current discharge, a difference not predicted by the theory.

A notable advance in the quantum theory of line spectra was made in 1918 by Bohr,[1] who worked out a logical basis for the intensity and state of polarization of the various fine structure lines. This theory he applied also to the Stark and to the Zeeman effect. Kramers (loc. cit.), working under Bohr, made a detailed application of Bohr's ideas to the Stark effect, in hydrogen and in helium, and to the fine structure of the lines, in these two gases. The agreement between theory and experiment, in the case of the Stark effect, is very remarkable. The position of the Stark effect components had already been predicted by Epstein[2] and Schwarzschild.[3] The advance made by Bohr and Kramers consisted in the correct prediction of the intensity and state of polarization of each component.

Kramers' work on the fine structure of the lines indicated that the intensity of the various components varied enormously with the strength of the electric field, especially in the case of the hydrogen series. Electric fields such as are found in the ordinary vacuum tube are evidently primarily responsible for the appearance of the lines, and especially for the change of appearance with varying physical conditions, as observed by Merton. The chief purpose of the present paper is to apply Kramers' theoretical results to the Balmer series, since Kramers himself made no detailed comparison except in one case to be mentioned presently.

[1] D. Kgl. Danske Vid. Selsk. Skr. natur og math. Afd., 8, R. IV., 1 and 2, 1918.

[2] Ann. d. Phys., 50, 489, 1916; 51, 168, 1916.

[3] Ber. Akad. Berlin, p. 548, 1916.

The articles by Sommerfeld, (1916) Bohr (1918), and Kramers (1919), are all very long and involved, especially the Kramers article. Consequently it is not possible to give a logical summary of the assumptions and conclusions, without making the present paper unduly long. Such material as is needed will be used without explanation, except by reference to the page number of the original article.

The Fine Structure of the Balmer Series, according to Sommerfeld.

As shown by equation (4), each spectral line consists of a number of components. In this equation $\alpha^2 = 5.308 \times 10^{-5}$ (using 6.555×10^{-27} for "h"). Sommerfeld (p. 68) used 5.30×10^{-5} for α^2. The equation, as applied to the Balmer series, may therefore be written (in terms of frequency-number)

$$\nu_3 = 5.822\left[\frac{1}{n''^4}\left(\frac{n_1''}{n_2''}\right) - \frac{1}{n'^4}\left(\frac{n_1'}{n_2'}\right)\right], \qquad (5)$$

where $n_1'' + n_2'' = n'' = 2$, and $n_1' + n_2' = n' = 3, 4, 5$, etc., and ν_3 gives the distance of the various components from the circle line. Any spectral line may be indicated by $(n_1'n_2', n_1''n_2'')$. The H_α circle line is therefore (03, 02), the H_β circle line (04, 02). The separation $(n_1'n_2',$ 11) $-$ $(n_1'n_2',$ 02) is known as the fundamental hydrogen separation. It is given by $5.822/2^4 = 0.3639$, or 0.3640 approximately. For this very important constant Paschen (p. 910) derived the experimental value of 0.3645 ± 0.0045, and used this value in all his calculations. The author has, however, used the theoretical value 0.3640. The H_α line thus consists of two sets of identical triplets (see Table I., and Fig. 1 *a*), separated by 0.3640ν ($= 0.1568$ Å.). The H_β line consists of two identical quadruplets, separated by 0.3640ν ($=0.0858$ Å.), etc. The Balmer series therefore consists of a doublet of constant $\Delta\nu$, the components of each member being themselves complex, but (as shown by equation 4) the total width of each component growing rapidly narrower, as n' increases.

A convenient method (used by Paschen) for labeling the various fine structure components is indicated in Table I., where the components of H_α, beginning at the red, are given in order, with the successive separations, in terms of Ångstroms. (See also Fig. 1 *a*.)

States in which $n_2 = 0$ are excluded, for this indicates no angular momentum, and the electron would therefore collide with the nucleus. The number of possible states is therefore only $n' \times n''$. Sommerfeld's first assumption as to intensity is that it is proportional to $(n_2'/n')(n_2''/n'')$, thus giving the maximum intensity (unity) to the circle line I_α. The

TABLE I.

1	2				3	4	5
Name.	n_1'	n_2'	n_1''	n_2''	Separation in Å.	Intensity Paschen 1.	Intensity Paschen 2.
I_c	2	1	0	2		2/6	small
I_b	1	2	0	2	0.0464	4/6	4/6
I_a	0	3	0	2	0.0155	6/6	6/6
II_c	2	1	1	1	0.0949	1/6	1/6
II_b	1	2	1	1	0.0464	2/6	2/6
II_a	0	3	1	1	0.0155	3/6	zero

intensities for the H_α components are given in the 4th column of Table I. Sommerfeld then makes the second assumption that, in an electron transition, the radial momentum never increases. This excludes the II_a line of each member of the Balmer series. He also makes the third

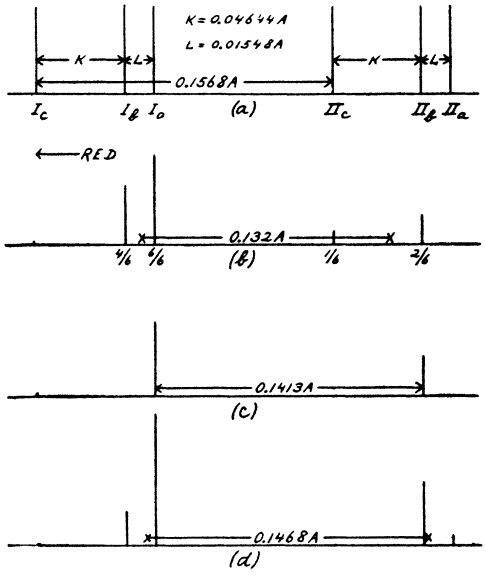

Fig. 1.

(*a*) H_α fine structure,—location only.
(*b*) Intensity relations according to Sommerfeld's theory.
(*c*) Intensity relations, with no electric field, according to Bohr-Kramers' theory.
(*d*) Intensity relations, with a field of 100 volts/cm., according to Bohr-Kramers' theory.
The crosses represent the centers of gravity of the two components of H_α.

assumption that an increase of angular momentum rarely if ever occurs. This indicates a very small intensity for the least refrangible member of each Balmer series line. The results, applied to H_α, are given numerically in Table I., column 5, and graphically in Fig. 1 *b*. They indicate a

doublet (each component of which is itself double), having a separation of 0.132 Å., and an intensity ratio of 3.3 to 1. Paschen, however, found that in the "4686" line the component III_a, corresponding to an increase of two units of radial momentum, appeared in the spark discharge with relatively great intensity. II_a, corresponding to an increase of one unit, was also very strong. Neither appeared in the constant current discharge. On the other hand, lines corresponding to an increase of angular momentum appeared faintly in both types of discharge. In fact, Sommerfeld made his third intensity assumption to agree with this observed fact.

SPECTRAL FORMULÆ FOR THE BALMER SERIES.

In measuring the wave-lengths of the Balmer series, as has been done by Curtis and others, what is actually observed is the apparent center of gravity of the complex line.[1] In order to interpret the results it is necessary to make assumptions in regard to the intensity, as well as the position, of the fine structure components. With such assumptions made, it is possible to compute, from the observed center of gravity of the line, the true wave-length of the circle component I_a. It is to this component alone that formulá (2) or (2′) applies. This is the procedure followed by Paschen (loc. cit.). Curtis however, in his 1919 article, applied (2′) directly to the original measurements. He also took α^2 as an undetermined constant, obtaining by a Least Squares solution a value of 15.48×10^{-5}, as compared to the theoretical value 5.308×10^{-5}. The author has found that an almost equally good agreement between the observed and computed wave-lengths can be obtained by using the theoretical value of α^2. There is however a definite divergence between theory and experiment which appears more clearly by handling the data in a different way, as indicated below.

Curtis uses other two constant and even three constant formulæ. Since the deviations from equation (1) are very small, it is to be expected that the addition of one or two additional constants, in almost any functional form, will result in a fairly good agreement, such as Curtis found. But formula (2), as applied to the Sommerfeld theory, has only one undetermined constant (N_0). Even this would be a determined constant, if we had accurate enough values of "h" and "e." α^2 is also a function of these quantities, but considerable changes in the assumed value of α^2 make but slight alterations in the computed frequency. Equation (2) is then practically a one constant formula.

The deviations of the observed lines from equation (1) are best exhibited

[1] Curtis says that he intended to set on the actual center of the line. The matter is discussed in a later section of this paper.

by computing a value of N_0 ($= N_\omega$) from each observed wave-length. The results,[1] taken directly from Curtis' 1919 paper appear in Table II.,

TABLE II.

1, n'.	2, λ (Air).	3, Error.	4, N_ω (1).	5, ΔN (1).	6, $\Delta\lambda$ (1).	7, ΔN (2).	8, $\Delta\lambda$ (2).
3.....	6562.793	0.0017	109,679.155	+0.402	−0.0251	+0.278	−0.0166
4.....	4861.326	0.0010	78.896	+0.143	−0.0063	+0.057	−0.0025
5.....	4340.467	0.0006	78.776	+0.023	−0.0009	+0.003	−0.0001
6.....	4101.738	0.0013	78.748	−0.005	+0.0002	−0.009	+0.0003
7.....	3970.075	0.0016	78.738	−0.015	+0.0005	−0.007	+0.0003
8.....	3889.051	0.0011	78.750	−0.003	+0.0001	+0.013	−0.0005

column 4. As this column shows, the values of N_ω become sensibly constant, beginning with $n' = 5$ (H_γ). Accordingly the average value of N_ω, using the last four values only, has been computed, and then the deviations from this average value (which is 109, 678.753). The results, in terms of frequency, are given in column 5, and in terms of Ångstroms, in column 6.

In a similar manner, formula (2′) has been applied to the Curtis data, using the theoretical value of α^2. (This is the author's own work.) Again it appears that N_ω is sensibly constant after the first two wave-lengths. Its average value, from the last four, is 109,678.351. In column 7 are given the deviations from this average, in frequency units, and in column 8, the deviations in Ångstroms. A comparison of columns 8 and 6 indicates a reduction of error to 66 per cent. for H_α, 40 per cent. for H_β, 10 per cent. for H_γ, and no sensible change for the others. The discrepancy for H_α is still however ten times the experimental error. It is thus quite clear that the application of relativity mechanics to the Balmer formula results in a definite reduction of the discrepancy between observed and computed values, but does not in any way obliterate the discrepancy. The explanation must therefore be sought in the fine structure of the lines.

To make a rigid test between theory and experiment, it is necessary to make definite assumptions as to the position and intensity of every fine structure component. It is then possible to treat each Balmer series line as a doublet, each member of which is complex. Knowing the structure of the red component of the doublet, it is possible to compute the frequency of the circle line I_α (always the most refrangible member of

[1] In the reduction to vacuum, Curtis uses the new figures of the Bureau of Standards. These will be used exclusively in the present article. Paschen uses older data, which are not so accurate, and therefore his vacuum values are not quite correct.

Table II., column 3, gives Curtis' estimate of the probable error of each line, in Ångstroms.

the red component) if the position of the center of gravity of the red component is known. This center of gravity, in turn, can be computed from the observed center of gravity of the entire line, knowing the separation of the centers of gravity of the two components of the doublet, and their intensity ratio. But these latter data depend on the exact assumptions made as to the intensity of the fine structure lines.

Paschen applied this general process to the analysis of his own measurements, using ostensibly the Sommerfeld theory as to the position and intensity of the fine structure components. He however made a number of simplifying assumptions, as well as one inadvertent error. The strict application of the Sommerfeld theory (using all three assumptions as to intensity) gives for the intensity ratio of the doublets, 3.3 to 1 (H_α), 3 to 1 (H_β), 2.8 to 1 (H_γ), 2.67 to 1 (H_δ), 2.57 to 1 (H_ϵ), etc., the limiting value being 2 to 1. The corresponding doublet separations are, 0.3130ν (= 0.1320 Å), 0.3489ν (= 0.0822 Å), 0.3587ν (= 0.0676 Å.), 0.3639ν (= 0.0613 Å.), 0.3640ν (= 0.0574 Å.), respectively. Paschen however used a constant intensity ratio of 2 to 1 for all lines, and a constant doublet separation of 0.3645ν. The distance of the circle line from the center of gravity of the red component is also variable, and has been used as such by the author. Paschen assumed the distance always equal to $1/4(I_a - I_b)$. This is incorrect even for the H_α line, and is due to Paschen's accidental assumption of an intensity ratio of 3 to 1 for I_a/I_b, instead of the correct 3 to 2 ratio. The error thus introduced is 0.0023 Å. for H_α. For the other lines it is practically negligible. The correct H_α structure, on the Sommerfeld theory, is shown in Fig. 1 *b*.

As has already been noted, Sommerfeld's assumptions as to intensity do not agree with experimental results, in the case of the helium lines. The discrepancies have now been explained by Kramers, who shows that the relative intensity of all fine structure components depends upon the exact strength of the electric field in the vacuum tube. This matter will presently be treated in detail. Another serious conflict between the Sommerfeld theory and observed facts is in the matter of the half-breadth of the red and violet components. Merton observed 0.028 Å. for H_α, and 0.045 Å. for H_β. A careful computation of the Doppler effect gave 0.023 Å. and 0.017 Å. for these widths. But on the Sommerfeld theory, the red component of H_α should be about 0.015 Å. wide, and the violet component 0.046 Å. wide, regardless of *any* Doppler effect. Conversely, for H_β, the Sommerfeld theory gives a width of only 0.005 to 0.014 Å., much less than the observed, with the full Doppler effect counted in.

Using all available data and the new figures for reduction to vacuum, the author has computed the position of the circle line, from the observed

center of gravity of the entire line. This has been done according to the strict Sommerfeld theory, and also on the assumption of a constant 2 to 1 intensity ratio for the doublet. In view however of the discrepancy of this theory with observations, in the case of H_α and H_β, it does not seem advisable to present the results in detail. The values of N_ω obtained from the various lines are as consistent as those of Paschen.[1] Using a 2 to 1 intensity ratio, but the theoretical value of the doublet separation, an average value for N_ω of 109,677.826 is obtained. Using the theoretical intensity ratios given previously, the value is 109,677.944. The Curtis and Paschen wave-lengths, treated separately, yield the same average by the first method, but slightly different averages by the second. Neither of these averages includes H_α, since this line requires individual treatment. It will be noted that the values of N_ω are somewhat higher than that of Paschen.[2]

THE BOHR-KRAMERS THEORY OF INTENSITY.

Bohr's new "Selective" principle (Auswahlprinzip) for obtaining at least a rough estimate of the intensity of the fine structure components is based on the idea that the actual orbit of the electron, in the initial and in the final state, can be considered as the sum of a number of harmonic vibrations. The intensity of an emitted line of any given frequency is then connected with the amplitudes of the harmonic vibrations of corresponding frequency in the initial and in the final state of the electron. The type of harmonic vibration (linear, circular, or elliptic) indicates the polarization (linear, circular, or elliptic) of the emitted line.

As applied by Kramers to the case of a strong electric field, the principle yields results in remarkable agreement with experiment. The intensity, as well as the state of polarization, of every component of the Stark effect, in the hydrogen and helium (enhanced) series is theoretically accounted for. The same principle, applied to the fine structure of

[1] P. 935, loc. cit. Paschen obtained a weighted mean of 109,677.691, and gives the probable error as ± 0.06, although the probable error, by the ordinary Least Squares formula is only ± 0.0145. The author, in all computations in this paper, has used only an unweighted average.

[2] All the computations of the present article had been completed, and the article partly written, when there appeared a brief paper by Herbert Bell (Phil. Mag., 40, 489, 1920) on the "Helium-Hydrogen Series Constants." The only point at which this paper overlaps the present work is in regard to the results just given. Bell uses both Paschen and Curtis wave-lengths, and the new reduction to vacuum. He however follows exactly the method of Paschen, assuming a 2 to 1 intensity ratio, and a constant doublet separation of 0.3650. Like Paschen, he uses the erroneous intensity ratio 3 to 1, for I_a/I_b. Bell also makes a computation with an assumed 3 to 1 intensity ratio for the doublet components. His results naturally differ slightly from those just presented due to the different method of making the fine structure corrections.

these series, with no electric field, indicates (Kramers, p. 355) that only those transitions are possible for which the angular momentum *increases* or *decreases* by $h/2\pi$, *i.e.*, $n_2' - n_2'' = \pm 1$. In the case of the Balmer series this indicates the presence of only *three* fine structure components for each member, contrasted to $n'(n'' - n' + 1)$ components on the Sommerfeld theory. They are I_a, I_c and II_b for H_α, I_b, I_d and II_c for H_β, I_c, I_e and II_d for H_γ, etc.

The intensity of each component is given by an expression (Kramers p. 356) involving Bessel functions. The results for H_α, on an arbitrary scale, are 5.00 for I_a, 1.36 for II_b, 0.04 for I_c. The true intensity of I_a is then taken as about one half of 5.00, because I_a is a circle line, and in the case of the Stark effect it was found that the theory gave too high values for the intensity, in the case of circle lines (due presumably to the various approximations introduced in the application). This conclusion was deduced by checking the results with the known fact that in the Stark effect, the polarized components into which an unpolarized spectral line is split will, when taken together, show no characteristic polarization in any direction. The results thus show that there may be errors up to possibly 100 per cent. in Kramers' computed intensities, but these are relatively small compared to the discrepancies in Sommerfeld's work, which were sometimes in excess of 1000 per cent.

The Kramers results for H_α are given in Fig. 1 *c*. They indicate a doublet separation of 0.1413 Å., and an intensity ratio of about 2 to 1. For H_β the results give a doublet separation ($I_b - II_c$) of 0.0822 Å., and an intensity ratio of about 1.25 to 1. The half-width of the H_β components, observed by Merton, is still less accounted for than on the Sommerfeld theory, although the H_α separation and intensity ratio checks very closely with Merton's experimental results.

Kramers (p. 359–378) then considers the effect of a weak electric field on the fine structure lines. His previous formulæ for the Stark effect hold only for strong fields. A rigid theory holding in all cases would be extremely complex, and has not yet been worked out. The results for a weak field indicate (as expected) that each fine structure component is broken up into a number of Stark effect components. Since the electric field is assumed very weak, the separation of these electric components may be neglected, and the intensity of any fine structure component may be judged by the sum of the intensities of all the Stark effect components composing it.

The calculations then show the extremely important result that various fine structure components previously missing may now appear, some of them with considerable intensity. In fact (Kramers, p. 364), while

previously there appeared only those transitions for which the angular momentum changed by one unit, we may now have the additional transitions for which the angular momentum remains unchanged, or changes by two units. If the intensities of the new components are small, compared to the original components, the intensity of the old components will be practically uninfluenced by the perturbing electric field. These new components, in the case of the helium lines, explain with one questionable exception the experimental observations of Paschen (see Kramers, pp. 372–376).

The equations for obtaining the intensity of the new components are given on page 367 of Kramers. They are very complex, and contain, it may be noted, several typographical errors. These errors may however be readily identified by comparing the expressions with those on pages 318–320, from which they were derived. Kramers computes numerical results for H_α and for Helium 4686 and 3203 only. The author has checked most of Kramers' calculations. The only serious error found is in the case of the II_α component of both H_α and Helium 4686, for which Kramers computes practically zero intensity, while the correct results are 1.588 and 0.115 respectively.[1] These intensities are for an electric field of 300 volts per cm. The intensity of the line varies as the square of the field intensity, and inversely as the fifth power of N. It also depends, in a more complex manner, on n' and n'', increasing very rapidly with increase in either or both.

The author believes that the last two sentences furnish the clue to the interpretation of all of Merton's results, in mixtures of hydrogen and helium.[2] Merton himself remarks (p. 310) "the only cause of broadening to be suspected would be . . . due to the influence of the electric field of neighboring charged particles on radiating atoms, operating in accordance with the Stark effect. It is true that this effect is greater for hydrogen than for other elements, but the effect in the case of helium is comparable in magnitude and the excellent agreement between the experimentally measured widths of helium lines and the widths calculated on the basis

[1] For H_α, R'^2 is 1.141 and 0.447 for the two components of II_α, *i.e.*, (03,11). For He 4686 the R'^2 of the five components of II_α, *i.e.*, (04,12), is 0.025, 0.039, 0.0149, 0.0189, and 0.0173, respectively. The Kramers results for R''^2 are correct. The author's corrected intensity for II_α of 4686 accounts better for Paschen's observed line, in the spark discharge, at 4685.687.

[2] The Balmer series, with the fine structure predicted by theory, seems to appear only in mixtures of hydrogen and helium. No attempt is made in this paper to explain the various effects noted by Merton in pure hydrogen, and in hydrogen containing a trace of impurity. The cause of these effects is undoubtedly to be looked for in the *irregular, local* fields of force of the surrounding atoms, as contrasted to the *general* electric field discussed here. It is only the helium atom which has practically no electron "affinity," and so no appreciable local field.

of the Doppler effect in the experiments of Buisson and Fabry would seem to leave little room for broadening of this type."

Using Kramers' results, this conclusion is not justified. The author has found that by assuming a uniform field of 100 volts per cm., such as has experimentally been found to exist in the hydrogen positive column, under a few mm. pressure, the effect for helium and for hydrogen is very different, and is quite capable of explaining the experimental results. It is not possible to give with authority the exact quantitative figures. In the case of H_β such a field produces a Stark effect splitting which is comparable in magnitude with the fine structure separation. For this line one therefore is effectively dealing with a "strong" electric field, to which the simpler Epstein-Schwarzschild formula applies. Moreover, the computed intensity of some of the new fine structure components is many times as great as the intensity of the strongest of the original components, whereas the formulæ used are intended only for the case where these new components are comparatively weak. When they are strong the original components themselves will have changed in magnitude by an amount comparable with the intensity of the new components, but Kramers has derived no formula for this increase. The actual relations are therefore only very approximate.

The results are as follows. For a field of 100 volts per cm., the total Stark effect width for He 4686 is 0.0085 Å. But the strong components are all near the center (Kramers, Plate III.) so that the observed broadening might appear much less. For He 3203, the breadth is 0.0092 Å. This should be observed, since the strong components are on the outside. The regular fine structure components of 4686 are all at intervals of 0.05 Å. or more (Paschen, p. 916), and the observed breadths 0.03 Å. or more. The electric fields in Paschen's work may therefore be much stronger than 100 volts per cm.

For H_α, a field of 100 volts per cm. gives a total possible Stark effect width of 0.0224 Å., but the outer components are much weaker than the central (Kramers, Plate I.) so that the effective half-width is probably less than half as great. Merton computes 0.023 Å. for the Doppler effect and observes 0.028 for the half-width. This is in reasonable agreement with theory, especially as the broadening due to the electric field and that due to the Doppler effect may not be simply additive. The only fine structure components that are really effective are still I_a and II_b so there is no effective broadening due to the fine structure. The exact results are shown in Fig. 1 *d*, where, according to Kramers' suggestion, the intensity of the new components is added to the neighboring old components. The figures then become (with corrections to

Kramers' computations previously noted) $I_a = 2.237$, $I_b = 0.577$, $II_a = 0.196$, $II_b = 1.096$. The intensity ratio for the doublet is $(2.237 + 0.577)/(0.196 + 1.096) = 2.18$ to 1, or exactly equal to Merton's observed value. The center of gravity of the red component is 0.0032 Å. to the red of I_a, while that of the violet component is 0.0023 Å. to the violet of II_b. The separation of the doublet is 0.1468 Å., compared to Merton's observed value of 0.1446 Å.

For H_β with a field of 100 volts per cm., the total Stark effect width is 0.0304 Å., and the strongest components are on the outside (Kramers, Plate I.) so that this value should represent the observed broadening. The Doppler effect is 0.017 Å., and if this is simply additive, the total width is 0.0474 Å., as compared to Merton's observed value of 0.045 Å. It is probable that 0.002 to 0.004 Å. should be added for the fine structure, making a total expected half-width of as much as 0.051 Å. Again however this assumes the Stark effect broadening and the Doppler effect broadening as simply additive.

The fine structure broadening of 0.002 to 0.004 Å. is the result of the author's computations, Kramers having done no work on this line. The original components, with their relative intensities are I_b (0.104), II_c (0.085), and I_d (0.002). The *new* components, due to an electric field of 100 volts per cm., with their intensities, are I_a (11.85), II_b (8.29), and I_c (1.72). We have thus, as previously noted, new components much stronger than the old, with no means of accurately computing the intensity change in the old. Assuming it to be the same as in the new components, we have the red member of the doublet composed of two almost equally strong lines I_a and I_b, with a separation of 0.0018 Å., together with the comparatively weak I_c line, while the violet member is composed of two strong lines II_b and II_c, separated 0.0036 Å. The intensity ratio is roughly $11.85/8.29 = 1.43$ to 1, while the separation[1] is about 0.0840, compared to Merton's 0.093 Å. (Merton himself thinks that this value may be too large.) Merton did not measure the intensity ratio for H_β but a mere visual inspection of the published photographs (p. 316) indicates that the ratio is much less for H_β than for H_α.

For H_γ the Stark effect broadening is 0.0435 Å., with again the strong components on the outside. As the total doublet separation is only about 0.068 Å., it is not to be expected that this line can be resolved, under any of the experimental conditions realized by Merton. Many of the changes of appearance observed by Merton, with varying chemical and electrical conditions, can thus doubtless be explained by changing

[1] This assumes the center of gravity of the violet component halfway between II_b and II_c, and of the red component at I_b (due to the influence of I_c.)

electric fields, interatomic if not general. That the electric field is competent to explain all observed half-widths, for resolved helium and hydrogen lines, seems evident in the light of the above figures.

THE VALUE OF THE RYDBERG CONSTANT N_ω.

We are now ready to return to the original problem of testing equation (3). The test consists of computing a theoretical value for the circle line and substituting this in equation (2). The values for N_ω ($= N_0$ of equation 2) should be constant, and may be compared to the values given in Table II.

As previously mentioned, the Sommerfeld theory of intensities yields a constant N_ω, provided H_α is excluded. The Bohr-Kramers theory is equally satisfactory. The results are given in Table III.

TABLE III.

1.	2, N_ω.	3, $r(\nu)$.	4, $r(\lambda)$.	5, N_ω.	6, $r(\nu)$
H_β Paschen.....	7.815	−0.006	+0.0003	7.665	+0.048
" Meissner.....	7.747	−0.074	+0.0033	7.597	−0.020
" Curtis.....	7.815	−0.006	+0.0003	7.665	+0.048
H_γ Paschen.....	7.851	+0.030	−0.0012	7.660	+0.043
" Curtis.....	7.800	−0.021	+0.0008	7.609	−0.008
H_δ Paschen.....	7.887	+0.066	−0.0025	7.642	+0.025
" Curtis.....	7.807	−0.014	+0.0005	7.561	−0.056
H_ϵ Curtis.....	7.821	±0.	±0.	7.571	−0.046
H_ζ Curtis.....	7.848	+0.027	−0.0010	7.587	−0.030
Average.....	7.821	0.027	0.0011	7.617	0.036

Column 2 gives the value of N_ω (the integral part 109,677 being omitted) using a constant intensity ratio of 2 to 1 for the doublet, but the theoretical separation.[1] In order to obtain the circle line, the center of gravity of the red component, in the case of H_β, is assumed at I_b, as explained in the previous note, *i.e.*, 0.0018 Å to the red of the circle line I_a. For H_γ the corresponding correction is about 0.0007 Å. For the other lines it is negligible.

On these assumptions, the average value of N_ω is 109,677.821, and the average residual, in frequency, is 0.027, as shown in column 3, or 0.0011 Å, as shown in column 4.

The same process has been repeated, using the true intensity ratio given by the Bohr-Kramers theory, *i.e.*, 2.18 to 1 for H_α and 1.43 to

[1] This separation is 0.0840 Å. for H_β, and 0.0674 for H_γ, with the electric field used. For the other lines the constant separation of $0.3640\,\nu$ is used, as the error thus introduced is negligible.

1 for H_β. The results for the other lines have not been determined as the computations are very laborious; but it is evident that the ratio is rapidly declining, and will reach unity in the limit. I have accordingly assumed ratios as follows, 1.2 to 1 for H_γ, 1.1 to 1 for H_δ, 1.05 to 1 for H_ϵ, and 1 to 1 for H_ζ. The results are given in column 5 of Table III. (where again the integral part 109,677 is omitted), and the frequency residuals in column 6.[1]

The final problem is to determine how the experimental results for H_α check with these values of N_ω. To do this it seems simpler to use the average N_ω already obtained to compute a theoretical value for the wave-length (in air) of the circle line of H_α. Using 109,677.821 for N_ω, we obtain 6562.8413 Å. Using 109,677.617, we obtain 6562.8535 Å. As previously deduced, using the Bohr-Kramers theory and 100 volts per cm., the center of gravity of the red component should be 0.0032 Å. to the red of the circle line. This gives for its theoretical position 6562.-8445 Å. or 6562.8567 Å. The average is 6562.8506. For the center of gravity of the red component Paschen observed 6562.853, while Meissner observed 6562.849. The average is 6562.851 which agrees exactly with the theoretical average. In other words, various theories as to the intensity of the electric field and the resulting intensity of the components of the lines lead to somewhat different expected results for the position of the red component of H_α, but the observed results also vary, and the various experimental and theoretical results all lie in the same region, and have the same average.

The second method of checking H_α is from the observed position of the center of gravity of the entire line. This position is 6562.797, according to Paschen, and 6562.793, according to Curtis. If 6562.8445 is the true position of the center of gravity of the red component, and if Merton's experimental value of 0.1446 Å. is assumed for the doublet separation (the theoretical value being about 0.1468 Å.), then Paschen's

[1] Curtis mentions that, in measuring the position of a line, he attempted to set on the actual center of the line, and not on its center of gravity. Paschen however says he attempted to set on the center of gravity. Bell calls attention to a slight systematic drift of Paschen's wave-lengths, as compared to Curtis'. There *is* such a drift, but it is doubtless due to the different reference standards used, and not to the method of setting. Thus if Curtis *really* set on the center of the line, his readings should be corrected (to a first approximation) by assuming a 1 to 1 intensity ratio of doublet components, instead of that actually used. This change in method would shift the $H\beta$ circle line by 0.0092 Å, from its predicted position on a 1.43 to 1 intensity ratio, or by 0.0158 Å., on a 2 to 1 ratio. Yet the Curtis and Paschen measurements agree for this line, (to 0.001 Å.), and differ by 0.004 Å. or less for all the others. It thus does not seem possible that Curtis and Paschen used essentially different methods of setting. If it *is* assumed that Curtis set on the actual center of the line, then, using only his values of wave-length, the average N_w is 109,677.524 and its constancy is about the same as before.

observation requires an intensity ratio of 2.04 to 1, while Curtis' requires 1.81 to 1. If 6562.8567 is the true value of the center of gravity, then Paschen's observation requires an intensity ratio of 1.42 to 1, while Curtis' requires 1.27 to 1. Meissner observed 1.4 to 1 ratio, while Merton observed 2.2 to 1.[1] With such discordant experimental results, it is hard to decide what ratio should be used, and it is evident that the value of the ratio depends greatly upon experimental conditions. A measurement of the center of gravity of the entire line is thus valueless, unless the intensity ratio, for the *same* conditions, is known. Moreover, the slightest change in the ratio makes a perceptible difference in the final comparison of theory and experiment. The only valid method at present available seems then that of using the directly observed center of gravity of the red component, and this, as shown, leads to a fairly satisfactory agreement of theory and experiment.

The various values for N_ω are summarized as follows,

Sommerfeld theory, 2 to 1 ratio	109,677.826
Sommerfeld theory, theoretical ratio	109,677.944
Bohr-Kramers theory, 2 to 1 ratio	109,677.821
Bohr-Kramers theory, theoretical ratio	109,677.617

These may be compared to previous results,

Paschen (Sommerfeld theory)	109,677.691
Curtis (empirical formulæ)	109,677.58 to 109,678.76

The author recommends for N_ω the value **109,677.7**, which is probably correct to 0.2.

The best value of e/m is 1.773×10^7,[2] and this, combined with 4.774×10^{-10} for e, and 96,470 for the Faraday,[1] gives 1.6636×10^{-24} grams for the mass of the hydrogen atom, and 1853 to 1, as the ratio of its mass to that of the electron. We have therefore

$$N_\infty = \frac{2\pi^2 me^4}{ch^3} = 109{,}677.7\left(1 + \frac{1}{1853}\right) = \mathbf{109{,}736.9 \pm 0.2.}$$

This may be compared to Paschen's determination (p. 936, loc. cit.) of 109, 737.18, using 1843.7 for the above ratio of M_H to m.

It has thus been shown that the quantum theory of line spectra, using the "Selective principle" of Bohr, leads, in the case of the Balmer series, to consistent values of N_ω, as well as to a satisfactory explanation of the

[1] On the assumption that Curtis set on the center of each line, thus giving 109,677.525 for N_w, we obtain 6562.8622 Å. for the center of gravity of the red component. For this Curtis' H_α value demands an intensity ratio of 1.09 to 1, as compared to a theoretical 1 to 1 ratio on this assumption. We again have consistent results, but a slightly lower value of N_w.

[2] Birge, PHYS. REV., 14, 361, 1919.

observed doublet separation, the observed intensity ratio of the components, and the observed half-width of the components.

THE BALMER SERIES IN MIXTURES OF H AND He AT HIGH PRESSURES.

An entirely different type of phenomena is that illustrated by the appearance of the Balmer series, down to $n' = 14$, in mixtures of H and He at 41 mm. pressure. Merton and Nicholson consider this important evidence against the entire Bohr theory of the hydrogen atom, but in view of the many exact quantitative agreements of this theory, little doubt can remain as to its general validity. It is therefore necessary to "explain" these observations. Assuming a *constant* temperature of 15° C., and a *constant* separation of the atoms, it appears, as stated by Merton and Nicholson, that the diameter of the ring (2.08×10^{-6} cm.) for $n' = 14$, is twice the distance apart of the atoms (1.0×10^{-6} cm.)

Qualitatively, all phenomena agree with the Bohr atom. Wood (loc. cit.) finds that, aside from the disturbing effects due to the secondary spectrum, the successive lines of the Balmer series appear as the pressure is lowered. Merton and Nicholson find that the higher members have relatively less intensity at high pressures. Wood finds that H_{20} has only 1/600,000 the intensity of H_α, in a long vacuum tube at 0.4 mm. pressure, while in the nebulæ the intensity decrement is much smaller. The Merton and Nicholson figures for the intensity decrement lead to 1/4,000,000 for this ratio.

It thus follows that, considering *only* those atoms which, at any instant, are radiating monochromatic energy, it is merely necessary that an extremely small fraction of this number need to be several times as far from all neighboring atoms as the average distance. With a Maxwellian distribution of velocities and distances, this seems easily possible. The question as to what fraction of the total number of atoms is at any instant emitting monochromatic radiation does not enter here. Except in the case of the "first resonance" line, this fraction also is believed to be very small. Furthermore, it is well known that the helium atom has practically no effect, either attractive or repulsive, on near-by electrons. This explains simultaneously why the predicted fine structure of the Balmer series appears *only* in mixtures of H and He, why the 12th member of the series can appear at all in such mixtures at high pressure, and why the higher members are extraordinarily sharp in such mixtures. Merton and Nicholson themselves remark the absence of broadening of the higher members, indicating an absence of any interatomic electric field, in spite of the proximity of the helium atoms.

There still remains the question of the temperature of the radiating

source. Because of the work of Buisson and Fabry[1] on the width of the helium lines, this temperature is now usually considered roughly that of the walls of the tube, and Merton uses this assumption, in his calculation of the Doppler effect for H_α and H_β. In view of the narrowing of these lines, at liquid-air temperature, it would appear that the assumption is certainly approximately correct for hydrogen, as well as for helium.

It seems to the author, therefore, that the well-known neutral effect of helium on neighboring electrons, together with the Maxwellian distribution of velocities, separations, etc., is quite sufficient to account for the experimental results thus far obtained. The fact that a small trace of impurity such as oxygen (see Wood, loc. cit.) seems necessary to the best production of the Balmer series would indicate that a strong field of force (due to the oxygen atom) is present under these conditions in the immediate neighborhood of the emitting atom. Yet this produces only a slight blurring of the emitted line (*i.e.*, frequency shifts of possibly one part in 50,000). All the more then can helium atoms be very close to the emitting center, without appreciably disturbing the emission.

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[1] Jour. de Phys., 2, Ser. 5, pp. 442–464, 1912.