THE DISTRIBUTION OF INTENSITY IN THE BROADENED BALMER LINES OF HYDROGEN

By E. O. Hulburt

Abstract

Broadening of the Balmer lines of hydrogen by condensed discharges.—(1) At various pressures, 48 to 250 mm, the intensity distribution was determined for $H\beta$, $H\gamma$ and $H\delta$ by photographing the spectra through a neutral wedge. In each case the broadening was symmetrical, amounting to about 60A for each line at 250 mm, but the curves gave evidences of structure characteristic of each line. The effect of a quenched gap in series with the tube was to increase the broadening, while inductance decreased it. (2) *In mixtures with He or* N_2, the broadening was the same as in hydrogen alone at the same total pressure. (3) *Stark theory of broadening* which relates it to the Stark effect of the electrical fields of the ionized atoms or the radiating atoms, *is given mathematical formulation* by assuming a probability law for the distribution of the atoms and ions and an inverse square law for the strength of the field, and introducing Sommerfeld's quantum expression for the Stark displacement. This gives $\log I_\lambda = \log [a/(\lambda_0 - \lambda)] - b/(\lambda_0 - \lambda)$, where $a = A\lambda\lambda_0 p^2 f$ and $b = B\lambda\lambda_0 p^{2/3} f$, where f is a known function of the quantum numbers. Comparison with experiment shows agreement as to the general form of the distribution curves. The great broadening produced by the condensed discharge is then due to the momentary high current density and corresponding large proportion of ionized atoms.

Neutral wedge cell, filled with an aqueous solution of a black dye, was found more convenient to adjust than the ordinary neutral glass wedge.

Introduction

UNDER usual excitation by a transformer or induction coil the lines of the Balmer series of hydrogen at low pressure are sharply defined although weak in intensity. When the gas pressure is increased to several hundred mm of mercury and when condensed discharges are employed, the Balmer lines increase in intensity and widen until almost unrecognizable. This broadening has received unusual attention from investigators because of the large magnitude and because of the importance of the hydrogen atom in theories of atomic structure. However, Rossi[1] seems to have been the first to indicate what now appears to be the true cause of the enhancement of the lines. As a result of his observations he stated, "It would seem that current density is a very important, if not the only,

[1] Rossi, Astrophysical Journal **40**, 232, 1914

factor in the phenomenon." The work of Stark on the modifications of radiations when the source of the radiations was subjected to an electric field, led to the suggestion that the broadening of spectrum lines might in some instances be attributed to the presence of electric charges in the vicinity of luminous atoms. This suggestion was given definite form by Merton[2] and by Nicholson and Merton[3] in an investigation of the intensity distribution across $H\alpha$, $H\beta$ and $H\gamma$ radiated from hydrogen at atmospheric pressure when excited by condensed discharges. A detailed analysis of the intensity curve of $H\alpha$ enabled them to conclude that the broadening was in close agreement with the results to be expected from Stark's observations of the electrical resolution of the line.

It seemed that an application of the recent theoretical work on the Stark effect of the Bohr hydrogen atom to the broadening problem would lead to a clearer understanding of the phenomenon. This has been attempted in the present investigation. After the intensity distribution had been measured across the hydrogen lines $H\beta$, $H\gamma$ and $H\delta$, stimulated by condensed discharges, for a pressure range from 48 to 250 mm of mercury, theoretical consideration of the radiations to be expected from a gaseous system of hydrogen atoms of the Bohr design mingled with charged particles, yielded a formula which gave substantial agreement with the observed intensity curves.

Experimental Details

Pure dry hydrogen, prepared from hydrochloric acid and zinc, was passed into the end-on discharge tube *d*, Fig. 1, made of glass with

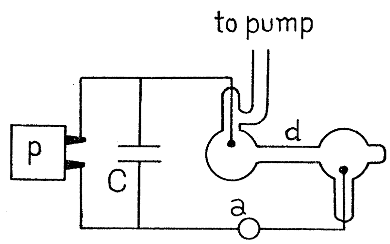

Fig. 1. Discharge tube and connections.

aluminum electrodes arranged out of line with the capillary, which was 4 cm long and 5 mm in diameter. The gas was excited by the discharges from a condenser *C* of capacity 0.0084 microfarads which received its power from a 1 kw, 25 kv, transformer *P*. The current through the tube was read by the thermo-galvanometer *a*. The current was in all cases

[2] Merton, Proc. Roy. Soc., **92**, 322, 1915

[3] Nicholson and Merton, Phil. Trans. Roy. Soc., **216**, 458, 1916

oscillatory, of frequency about 0.67×10^6 per second as measured by a wave-meter. The spectra were photographed with a glass prism spectroscope of the Littrow type, the dispersion at 5000, 4000, and 3600A being about 40, 20, and 15A per mm, respectively.

To obtain the distribution of intensity across the line a neutral wedge was placed before the slit of the spectrograph. A complete description of the neutral wedge method and a discussion of the theory is found in the papers by Merton, already referred to, in which the advantages and possibilities of the method and the precautions to be observed are clearly set forth. In the present instance a wedge was constructed by cementing glass plates together with sealing wax to form a cell with two wedge shaped compartments, Fig. 2. The angle α of the wedge was 17°, and the external dimensions of the cell were $1.5 \times 2.5 \times 3.5$ cm. One compartment

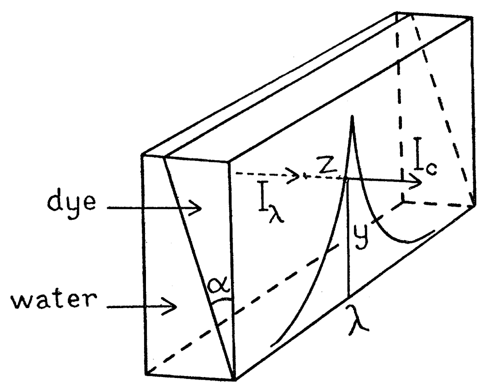

Fig. 2. Wedge cell.

was filled with water and the other with an aqueous solution of a black dye ("Erie Black, G×OO," National Anilene and Chemical Co., New York). The concentration of the solution was varied until the photographs had the best appearance. The advantage which this type of wedge had over a neutral glass wedge lay in the ease of construction and the freedom of adjustment to the experimental conditions.

The neutral wedge method. When the neutral wedge is interposed between a spectral line of finite width and the photographic plate, let us suppose that the plate records an image of the line of the form shown, for illustration, in Fig. 2. This figure indicates that the wedge was contiguous to the plate, whereas in reality the wedge was in front of the slit of the spectrograph, but the two cases are of course identical so far as the present discussion is concerned. We now seek the determination of the true intensity distribution curve of the line from the photographic image found by means of the wedge. At all points on the edge of the image the intensity of the light has a constant value I_c, since under the condition of the exposure, light of less intensity does not produce a perceptible effect on the photographic plate. Let the coordinates of a point on the contour of the image be (λ, y), where y is measured from the thin edge of the wedge. Let z be the thickness of the wedge at this point. If I_λ is the undiminished intensity of the light of wave-length λ at this point, $I_c = I_\lambda e^{-kz}$, or

$$I_c = I_\lambda e^{ky \tan \alpha}, \tag{1}$$

where k is the absorption coefficient of the material of the wedge for radiation of wave-length λ. I_c is a constant, and we shall assume k is a constant throughout the range of wave-lengths of the broadened line. Therefore from (1) the values of I_λ in arbitrary units may be determined for each value of λ merely by measuring y for each λ, and in this way the true intensity distribution curve may be obtained. Actually in the present experiment a variation of this procedure has been adopted; namely, I_λ was determined as a function of λ throughout the line from a theoretical consideration. From this function the form of the intensity distribution curve to be expected after the spectral line had passed through the wedge was calculated by means of (1) and a comparison was then effected between the theoretical and the experimental intensity curves.

Experimental Results

Spectra of hydrogen were photographed through the neutral wedge for pressures 48, 112, 160 and 250 mm of mercury. These are shown in Plate 1, *a*, *b*, *c* and *d*, respectively. The currents through the gas for each pressure were 1.2, 2.3, 2.8 and 4.1 amperes, respectively. The time of exposure was 20 minutes in each case. The contour of the image of the lines was in general convex to the wave-length axis for all the lines, the curves as seen in the reproduction being fairly smooth. On the original plates, however, the contours gave unmistakable evidence of structure in the line. $H\beta$ was noticeably a close hazy doublet at the apex; $H\gamma$ and $H\delta$ gave evidences of slight wings symmetrically placed on either side; and $H\gamma$ exhibited a bright central core which was lacking in the case of $H\delta$. These details are indicated more clearly in the heavy line drawings in Fig. 3 of the images for a pressure of 250 mm reduced to a uniform scale of wave-lengths. The facts concerning the structure of $H\beta$ and $H\gamma$ when broadened have been mentioned before.[1,2] If the images of $H\beta$ and $H\lambda$ were enlarged until their highest ordinates were equal to the maximum ordinate of $H\alpha$ it would be seen that the widening for a specified pressure increases with the series term number of the line.

THEORETICAL

We proceed to a consideration of the simple theory of the general form of the curves and reserve for a later paragraph a suggestion for a more detailed explanation.

Intermingled with the radiating hydrogen atoms in the discharge tube are charged particles. These charged particles may be electrons, ions or even the component charges of a neutral atom. As a result the radiating atom finds itself in an electric field and therefore, in agreement with the observations of Stark, instead of emitting a single line it gives forth a group of lines whose displacement from the parent line is directly

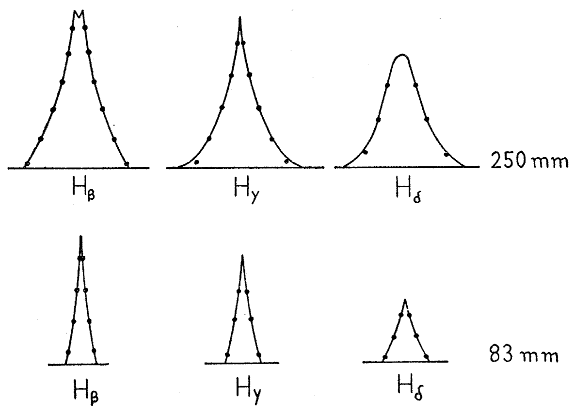

Fig. 3. Broadening curves; observed (full lines) and computed (dots).

proportional to the strength of the electric field. Throughout a finite interval of time a radiating atom may be expected to be subjected to fields of a wide range of intensities and in spite of the many complexities of the case it seems reasonable to suppose that the average over a considerable length of time of the influence of the electric fields on a large number of radiating atoms will be in accordance with a probability law. In the following paragraphs these ideas are couched in mathematical terms.

The hydrogen gas in the path of the condensed discharges is largely atomic and is composed of electrons and of charged and neutral, luminous and quiescent atoms. Since ionization is probably essential to luminosity under the conditions of the discharge we cannot be far wrong in assuming that the number of luminous atoms and the number of the charged particles are of about the same order of magnitude. J. J. Thomson[4] has estimated the ratio of the number of ions to the total num-

[4] Thomson, "Conduction of Electricity Through Gases," 1906, p. 83

ber of molecules in a gas during the passage of an electric current to be about 10^{-14} in a certain instance. In the present experiment this ratio was probably much greater, because condensed discharges were used, but we may estimate with safety that the ratio was not greater than, say, 10^{-6}. The conclusion is that the number of both luminous atoms and charged particles was small compared to the total number of atoms present.

Let the total number of atoms per unit volume be ν, of which a fraction q contribute to the radiation. Let the distance from a luminous atom to a charged particle be denoted by δ. It is assumed that the number of luminous atoms ν_1 per unit volume which are at a distance δ from a neighboring charged particle, is given by the probability relation[5]

$$\nu_1 = A\nu\delta^2 e^{-B\delta^2}. \tag{2}$$

In order to avoid needless complication we simplify matters by assuming that the luminous atoms are the charged particles. This does not materially affect the argument because we are interested in the orders of magnitude of the numerical constants and not in their precise values. On this assumption we may write $\int_0^\infty \nu_1 d\delta = q\nu$; hence, $A = 4q\sqrt{B^3/\pi}$. If δ_m is the average distance between luminous atoms, then

$$\delta_m = 4\sqrt{\frac{B^3}{\pi}}\int_0^\infty e^{-B\delta^2}\delta^3 d\delta = \frac{2}{\sqrt{\pi B}}.$$

Also $\delta_m{}^3 = 1/q\nu$. Therefore $A = 2^5 q\nu/\pi^2$ and $B = 4q^{2/3}\nu^{2/3}/\pi$. ν depends on the pressure and may be written $\nu = 4\times10^{19}p/760$, where p is the pressure in mm of mercury. Introducing these values into (2) leads to

$$\nu_1 = \alpha p^2\delta^2 e^{-\beta p^{2/3}\delta^2}, \tag{3}$$

where $\alpha = 2^5/\pi^2\left(\frac{4\times10^{19}}{760}\right)^2 q$ and $\beta = 4/\pi\left(\frac{4\times10^{19}}{760}\right)^{2/3} q^{2/3} = 5\times10^{11} q^{2/3}$.

Making use of the estimated maximum value of q, i.e. 10^{-6}, the maximum value of β does not exceed 10^7.

The experiments of Stark[6] have demonstrated that in the case of the Balmer lines of hydrogen the displacements of the Stark components are closely proportional to the strength of the electric field. In his theoretical treatment of the electrical resolution of the radiations from the Bohr model of the hydrogen atom Sommerfeld[7] has derived a general

[5] Jeans, "Dynamical Theory of Gases," 1904, p. 28

[6] Stark, Ann. der Phys. **48**, 193, 1915

[7] Sommerfeld, "Atombau und Spektrallinien," 1922, p. 357.

relation for the displacement of any component, which is in agreement with Stark's data, namely,

$$\lambda_o - \lambda = \frac{3hF}{8\pi^2 mE} \frac{\lambda\lambda_o}{c} f\,, \tag{4}$$

where f is a function of the quantum numbers. The exact value of f is known; it differs for each component. λ_o is the wave-length of the parent line; λ is the wave-length of the component when the intensity of the electric field is F; h is the Planck constant; m the electronic mass; E the nuclear charge, and c is the velocity of light in vacuum. Since the Stark components are symmetrically placed and equally displaced on either side of the parent line the absolute value of $\lambda_o - \lambda$ is used in (4). In the problem under discussion the luminous atom is conceived to be subjected to the electric field of the charge e on the neighboring atom a distance δ away. The strength of the electric field is e/δ^2, the dielectric constant of the medium being unity, and if δ is large compared to the diameter of the atom the field is approximately uniform over the luminous atom. We thereupon replace F by e/δ^2 in (4) and solve for δ^2. This yields $\delta^2 = \alpha'/(\lambda_o - \lambda)$, where $\alpha' = 3he\lambda\lambda_o f/8\pi^2 mEc$. Taking f to be of the order of 10 and putting $\lambda = \lambda_o = 5000$A, we find α' to be of the order of 10^{-11}. Upon substitution of the expression for δ^2 in (3) we obtain

$$\nu_1 = \frac{a\alpha' p^2}{(\lambda_o - \lambda)} e^{-[\beta\alpha' p^{2/3}/(\lambda_o - \lambda)]}. \tag{5}$$

It must be noted that in equating F to e/δ^2 we have tacitly assumed that the field was due to a single charge. Actually the electric field at any point in the gas was the resultant of the fields of a swarm of charged particles of both signs in the vicinity of the point. This indicates that the right hand side of (5) and the exponent should each be multiplied by some fraction.

We may now assume that the intensity I_λ of the radiations of wave-length λ is proportional to ν_1, and write $I_\lambda = \alpha''\nu_1$. Hence from (5)

$$I_\lambda = \frac{a\alpha'\alpha'' p^2}{(\lambda_o - \lambda)} \quad e^{-[\beta\alpha' p^{2/3}/(\lambda_o - \lambda)]}. \tag{6}$$

The quantity $\beta\alpha' p^{2/3}$, according to our numerical estimates of β and α', is a small quantity, certainly never greater than 1/10 for pressures of the order of one atmosphere, and probably much less. We may therefore replace the exponential term of (6) by unity without appreciable error unless the absolute value of $\lambda_o - \lambda$ expressed in angstrom units be less than 1/10. Eq. (6) then becomes, to a close approximation,

$$I_\lambda = gp^2/(\lambda_o - \lambda), \tag{7}$$

where $g = \alpha\alpha'\alpha''$ and is approximately a constant across the broadened line. From (7) the line may be expected to widen with pressure. When I from (6) is plotted in arbitrary units against λ a curve of the form given by the heavy line of Fig. 4 is obtained. The curve is obviously not drawn to scale. At λ_o, I_λ is zero and the distance apart of the maxima is less than 0.1 A. This crevice in the intensity curve is perhaps beyond the reach of detection by experiment, and probably is of no physical significance. It merely results from the refusal of Eq. (6) to admit the possibility of there being any atom at all which emits the unaffected wave-length λ_o. In regard to the approximate formula (7), the intensity curve conforms closely to that of formula (6) except n the small interval

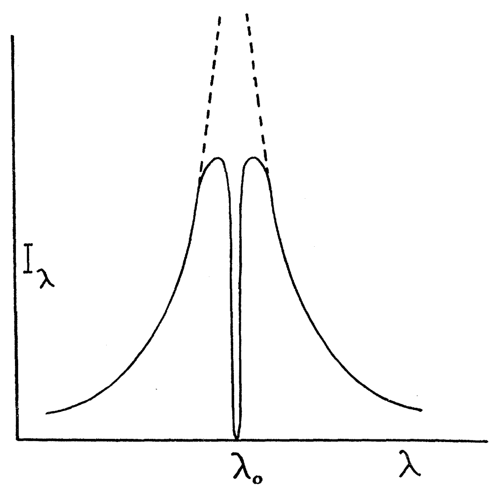

Fig. 4. Theoretical broadening curve.

between the two maxima in which the approximate formula is invalid. Ignorance of the exact physical conditions renders it difficult to attempt to derive an expression for the intensity at wave-length λ in terms of the intensity at the center of the parent line. We content ourselves therefore with formula (7) which affords relative values of I_λ for regions neither too near nor too remote from λ_o.

It remains to determine the equation of the intensity curve after the light has traversed the neutral wedge. This is obtained by eliminating I_λ between (1) and (7). There results

$$\lambda_o - \lambda = (gp^2/I_c)e^{-ky \tan \alpha}. \quad (8)$$

Comparison Between Theory and Experiment

Drawings of the enlarged images of the lines were made and reduced to a uniform wave-length scale. These are shown by the full lines of Fig. 3

for $H\beta$, $H\lambda$, and $H\delta$ at pressures 250 and 83 mm, which were plotted with values of y in arbitrary units as ordinates against values of $\lambda_0 - \lambda$ in angstrom units as abscissas. The constants g/I_c and $k \tan \alpha$ of Eq. (8) were determined from two observed points on the contour of $H\beta$ at a pressure 250 mm, and points on the intensity curve were then calculated. To obtain the theoretical curves for the other lines and pressures it was only necessary to readjust the quantity g/I_c of Eq. (8). This was permissible because the intensities were in arbitrary units. The calculated points are shown by the dots of Fig. 3. Similar comparisons were affected for all the other lines, and in all instances good agreement was found between the general forms of the observed and theoretical intensity curves.

Structural detail in the broadened line. The theoretical ideas thus far advanced in explanation of the general form of the intensity curve will not suffice to account for the evidences of structure observed in the broadened lines. A more detailed consideration is necessary. Merton[2] has supplied this by drawing attention to the close correspondence between the Stark components of a line and the form of the intensity distribution curve. To show this the p and s components of the electrical resolution of $H\beta$, $H\lambda$ and $H\delta$ as determined by Stark[8] are given in Fig. 5. It needs only a glance at these components to see that the $H\beta$ radiations

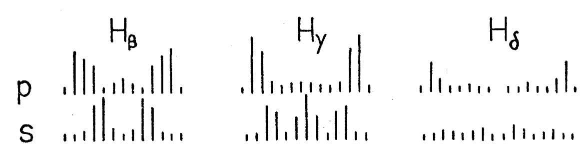

Fig. 5. Stark effect components.

from a large number of hydrogen atoms subjected to a wide range of electric fields will result in a widened line with perhaps a weak minimum at the center. In the cases of $H\lambda$ and $H\delta$ we should expect a widened line with more or less prominent wings, the center of $H\lambda$ being more brilliant than the center of $H\delta$. As far as can be judged these conclusions are in agreement with the appearance of the photographic images of the lines.

The role of the condensed discharge. As an outcome of the views set forth in explanation of the broadening, we are led to an understanding of the role played by the condensed discharge. In the condensed discharge the current density is very great for a short interval of time at the commencement of the discharge. It may easily amount to several hundred amperes. A gas which is stimulated by such a discharge emits

[8] Sommerfeld, loc. cit., p. 357

radiations characteristic of those caused by the passage of heavy currents. The luminous atoms in such a case are in the midst of a vast number of charged particles and a relatively large number may be expected to be subjected to strong electric fields. This results in the widening of the lines. On the other hand if a steady current, either direct or alternating, traverses the gas the current density never attains very high values and the charges present in the gas are never very numerous. Therefore the luminous atoms rarely experience strong electrical fields and no marked broadening of the lines occurs.

The effect of the quenched gap. The photographs *e* and *f* of Plate I indicate the increase in width of $H\beta$ occasioned by the introduction of a quenched gap in series with the tube. The pressure of the hydrogen was 130 mm, the current 2.1 amperes and the time of exposure 20 minutes in each case. For *e* the quenched gap was used, for *f* the discharge took place directly through the tube without the gap. The effect of the gap in producing widening was more marked at the lower than at the higher gas pressures. The insertion of the gap enabled the charges to accumulate on the condenser plates to higher potentials, so that when the discharge occurred a greater current than otherwise passed through the tube. The current was rapidly damped by the quenching action of the gap. As a consequence the gas was stimulated at each discharge by abrupt pulses of current more intense than those which occurred without the gap, even though the currents read by the thermogalvanometer were the same in the two cases. The stronger current pulses produced the greater broadening. The reason that the gap produced less effect for high gas pressures was simply that in those cases the tube itself quenched the discharge to a greater extent.

The effect of inductance. A coil of inductance 2.2×10^{-5} henries in series with the discharge tube reduced the widths of the broadened lines. An illustration of this is afforded by the photographs *g* and *h* of $H\beta$, *g* taken with the coil and *h* without the coil. The current was 3.0 amperes, the gas pressure 140 mm, and the time of exposure 11 minutes in each case. The frequency of the oscillatory discharge with the inductance was 1.2×10^5 and without it was 6.7×10^5; these were measured with a wavemeter, the tuning being of course very broad because of the resistance of the tube. The inductance served to distribute the discharge over a longer interval of time so that the pulses of current were of less intensity and therefore the spectrum lines were narrower than when the inductance was absent. The fact that an inductance will reduce or suppress entirely certain lines excited by spark discharges, has been known for a long time, but it appears that in some instances the electrical conditions of the

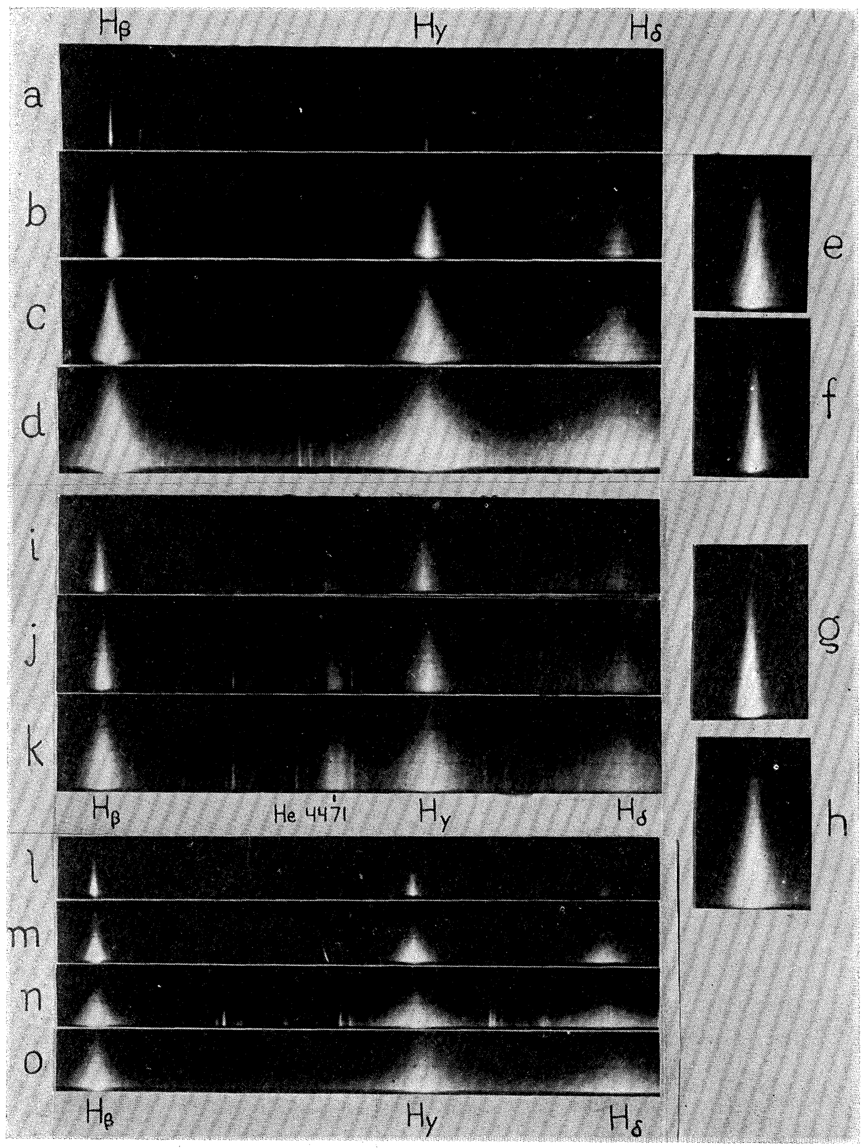

Plate I. Broadening of the Hydrogen lines by condensed discharges.

experiments have not been described in sufficient detail to enable possible explanations to be advanced.

Mixtures of Hydrogen with Helium and Nitrogen

Mixtures with helium. It was found that the Balmer lines of hydrogen at a relatively low pressure were broadened when the pressure was increased by the addition of an inert gas such as helium or nitrogen, in the same manner as by the addition of more hydrogen. Photographs *i*, *j* and *k* show the effect of helium. The data for these photographs are given in Table I. The helium contained a trace of nitrogen but this probably

Table I

Data for photographs i, j, and k

	Pressure of hydrogen	Pressure of helium	Current	Time of exposure
i	29 mm	79 mm	1.2 amp.	20 min.
j	29	188	3.0	20
k	29	380	4.2	20

had no effect in the present experiment. The enhancement of the hydrogen lines caused by the helium was to be expected from the views already outlined. Several factors, however, must be considered. The introduction of the inert gas increased the break-down potential of the discharge tube. A violent discharge thereupon ensued and a great number of charged particles were produced in the luminous gas with consequent enhancement of the Balmer lines. The charged particles came apparently from ionized hydrogen rather than from helium, since even with partial pressures of 380 mm of helium and only 29 mm of hydrogen the helium lines were of less intensity than the hydrogen lines. This of course was to be ascribed to the high resonance and ionization potentials of helium as compared with those of hydrogen, and to the fact that the higher the ionization potential of an element the greater is the difficulty with which it can be excited to emit its line spectrum.[9]

Mixtures with nitrogen. The enhancement of the Balmer lines from hydrogen mixed with nitrogen is shown by photographs *l*, *m*, *n* and *o*. The flatness of the contours of these lines resulted from the use of a neutral wedge of greater optical density than the one used for the other photographs. The conditions under which these were taken are given in Table II. It is interesting to notice the striking similarity of photographs *n* and *o* which were taken with the same total pressures but with quite different partial pressures of the component gases. The ionization potential of nitrogen is somewhat above that of hydrogen. Some of the

[9] Saha, Phil. Mag. **41,** 268, 1921

resonance potentials, however, are slightly lower than those of hydrogen and therefore it might be supposed that the nitrogen lines would appear nearly as prominently as the hydrogen lines. This does not seem to be the case in this experiment as indicated by spectrogram *k*. However, little can be said with certainty on this point because there is no criterion for the relative intensities of the spectrum lines of different elements.

Of the possible causes of broadening of spectrum lines recognized at the present time only two seem to be of sufficient potency to effect the relatively large widening noticeable in many enhanced lines. These two causes are the electric and magnetic fields. In the present experiments

TABLE II

Data for photographs l, m, n, o

	Pressure of hydrogen	Pressure of nitrogen	Current	Time of exposure
l	85 mm	0 mm	2.3 amp.	20 min.
m	85	55	2.5	20
n	85	115	3.0	20
o	200	0	3.0	20

as well as in all usual cases of broadened lines the Zeeman effect may be ruled out, although it may be possible to devise conditions in which the Zeeman effect is operative. This suggests that the Stark effect is the cause of most cases of broadening of spectrum lines, or more precisely, that the broadening is due to the electric fields of the charged particles which are produced by the same vigorous stimulation which brings into existence the broadened line. The results of many experiments, among which may be mentioned those of Hemsalech and de Gramont,[10] point to this conclusion.

I take pleasure in thanking Dr L. I. Shaw of the Bureau of Mines for a gift of helium.

PHYSICAL LABORATORY,
UNIVERSITY OF IOWA,
January 14, 1923[11]

[10] Hemsalech and Gramont, Phil. Mag. **43,** 287 and 834, 1922

[11] The paragraphs dealing with the effects of a quenched gap and of inductance were added February 7, 1923.

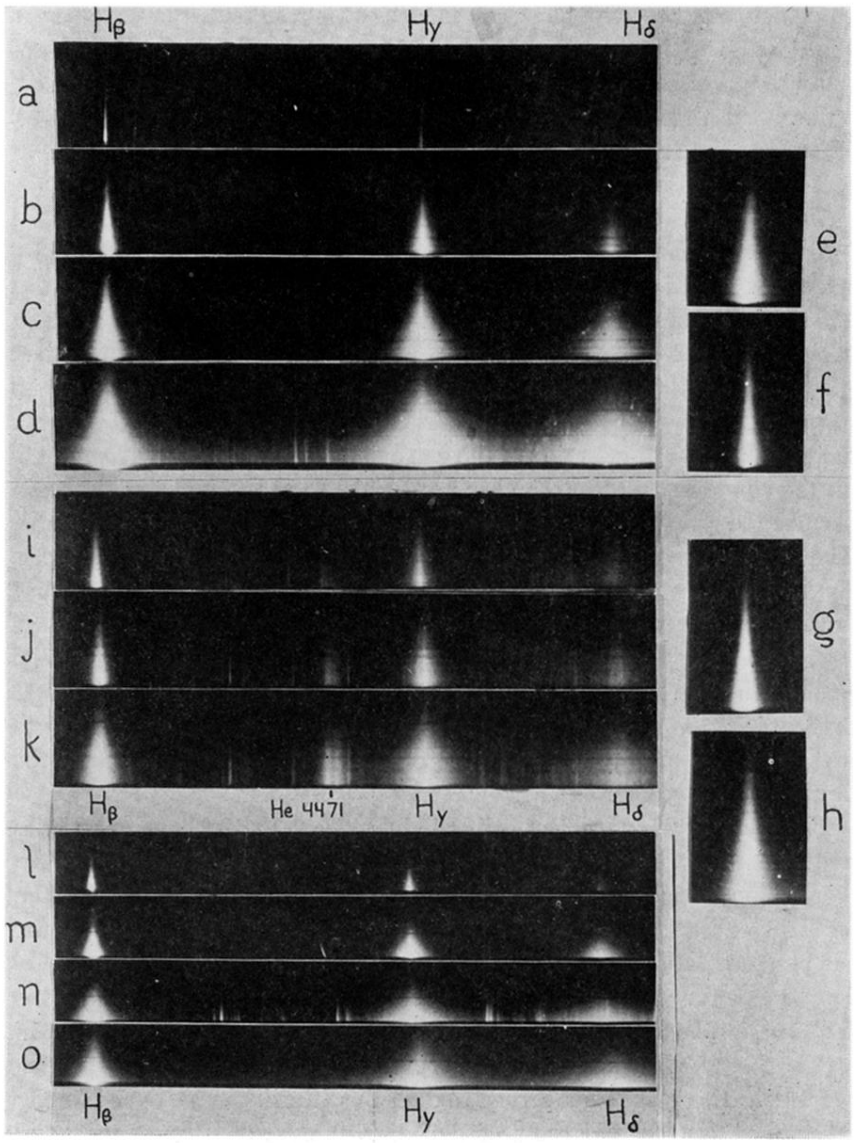

Plate I. Broadening of the Hydrogen lines by condensed discharges.