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X. *On the Distribution of Intensity in Broadened Spectrum Lines.*

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Communicated by Prof. A. Fowler, *F.R.S.*

[Plate 2.]

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Contents.

(I.) *Introductory.*

It is a curious fact that although our knowledge of the structure of the finest spectrum lines may now be said to rest on a secure theoretical and experimental basis, little is known of the distribution of energy in the broadened spectrum lines which are produced under certain conditions of excitation, or the exact circumstances which control their broadening. The researches of Lord Rayleigh,* Michelson,† Buisson and Fabry,‡ and others have shown that in gases at low pressures, when excited by uncondensed electric discharges, the width of the spectrum lines emitted can be accounted for completely and satisfactorily by the translatory motion of the

* 'Scientific Papers,' vol. I., p. 183; 'Phil. Mag.,' 29, p. 274, 1915.

† 'Phil. Mag.,' 34, p. 280, 1892; 'Astrophys. Journ.,' 3, p. 251, 1896.

‡ 'Journ. de Physique,' vol. 2, p. 442, 1912.

radiating particles, in accordance with DOPPLER'S principle. Measurements of the width of such lines are carried out with the interferometer, the measurement consisting of a determination of the limiting order of interference at which fringes can be seen. This limiting order of interference is given by the equation $N = K (M/T)^{1/2}$ where N is the limiting order of interference, M the mass of the luminous particle in terms of the hydrogen atom, T the absolute temperature and K a constant. This equation is derived from a consideration of the Doppler effect produced by a distribution of the velocities of the radiating particles in accordance with MAXWELL'S law, and its experimental verification by BUISSON and FABRY shows not only that under the conditions specified the widths of the lines are completely accounted for, but also that the distribution of intensity in the lines is given by the well-known probability law. Under these conditions it is further shown that the limiting order of interference is constant for all lines and all series of the same element. Thus the same value of N is found for the helium and the parhelium series, and in the same manner for the Balmer series and lines of the secondary spectrum of hydrogen.

With any departure from the specified conditions of low pressure and excitation by uncondensed electric discharge the law breaks down, and the lines broaden in an apparently anomalous manner. The characteristics which lead RYDBERG to adopt the terms diffuse and sharp series appear, the higher members of a series undergoing the greater degree of broadening. Matters are complicated by the fact that the broadening is in many cases unsymmetrical, and in addition we must take into account the fact pointed out by ROYDS,* that different members of the same series may be unsymmetrically broadened in opposite directions. Thus in the case of the first subordinate "triplet" series of barium, the members consisting of triplet and satellites at λλ 5819–5424 are all unsymmetrically broadened towards the red, whilst the members of the succeeding triplet (and satellites) and λλ 4493–4264 are unsymmetrically broadened towards the violet. ROYDS shows that similar phenomena occur in the spectra of calcium and strontium, and points out the importance of the phenomena in relation to the pressure shifts of the lines in question. There can be no doubt of the intimate relation between the direction of the asymmetry and the pressure shift, since it has been shown by ST. JOHN and WARE, FABRY and BUISSON,† and by GALE and ADAMS‡ that iron lines which broaden unsymmetrically towards the red are displaced by pressure towards the red, whilst lines which are unsymmetrically broadened towards the violet are displaced by pressure towards the violet. It is well known that broadening of spectrum lines can be produced either by an increase of the pressure of the luminous gas or by the use of highly condensed discharges as a means of excitation, and although the two conditions are different

* 'Astrophys. Journ.,' 41, p. 154, 1915.

† 'Astrophys. Journ.,' 36, p. 14, 1912; 31, p. 111, 1910.

‡ 'Astrophys. Journ.,' 37, p. 391, 1913.

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the phenomena of broadening which result appear to be similar. In a previous investigation it has been pointed out by one of the authors that from a consideration of the general characteristics of the broadening it appears difficult to refer the phenomena to the movements of the luminous particles as a whole, but rather that effects more intimately connected with the problem of radiation must be concerned. A recent suggestion by STARK* as to the cause of the broadening appears to be in harmony with the experimental results at present available.

(II.) *The Stark Effect in Relation to the Broadening of Spectrum Lines.*

STARK† has found that when a luminous source is placed in a powerful electric field the radiations are resolved into components in a manner analogous to the Zeeman effect in a magnetic field. The separation of the components in an electric field appears to be related in some way to the atomic weight of the element, the greatest effect being observed in the case of the Balmer series of hydrogen, and the diffuse series of helium. The separation is of another order of magnitude to the corresponding magnetic separation. Thus at $\lambda = 4000$ Å.U. the separation of the outer components of a normal Zeeman triplet in a field of 30,000 Gauss is about 0·5 Å.U., whilst for the hydrogen line H_γ in an electric field of 30,000 volts $\times$ cm.$^{-1}$, the outermost components are separated by 13·0 Å.U. STARK considers that the broadening of spectrum lines at high pressures and under powerful conditions of electrical excitation is intimately connected with the electrical resolution of the lines, being in fact due to the electric effect of neighbouring atoms on the luminous particle. The phenomena appear to be strictly analogous. STARK also points out that the electrical separation of the components increases with the term number in a series, just as the broadening also increases. The electrical separation is greatest for lines of diffuse series, which also undergo the greatest broadening. Further, lines in the spectra of helium and lithium which are unsymmetrically broadened are also unsymmetrically resolved in the electric field.‡

It is evident that in order to obtain further evidence it is necessary to determine experimentally the distribution of intensity in the broadened spectrum lines, since we may predict (on this view) from the separation and intensity of the components in an electric field, the distribution of intensity to be expected in the broadened spectrum lines. In a previous communication§ a method of investigating the distribution of intensity in broadened spectrum lines was described, and it was shown that the results

* 'Elektrische Spectralanalyse Chemischer Atome,' 1914. See also 'Ann. der Phys.,' No. 18, p. 193, 1915, in which the latest results for the Balmer series of hydrogen are given.

† *Loc. cit.* A valuable discussion of the subject has recently been published by FULCHER ('Astrophys. Journ.,' 41, p. 359, 1915).

‡ Reference may be made to the recent work of A. J. DEMPSTER, 'Ann. der Phys.,' 47, p. 791, 1915, who has investigated the breadth of spectrum lines with the interferometer, a method which the writers consider to be unsuitable for reasons given below.

§ 'Roy. Soc. Proc.,' A 92, p. 322 (1916).

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obtained for the hydrogen lines H_α, H_β, and H_γ were qualitatively in accordance with the intensity distribution to be expected on the view that the electric field of neighbouring atoms was responsible for the broadening. The present investigation is concerned with the quantitative determination of the distribution of intensity in broadened spectrum lines, with the view of throwing some further light on the nature of the broadening and the circumstances which control it.

(III.) *The Methods of Measurement.*

It is at once evident from the complex nature of the phenomena that a measurement of the limiting order of interference at which fringes can be seen for the broadened lines will be of little value in determining the intensity distribution. If the intensity distribution could be exactly predicted on theoretical grounds, it might be possible to verify the theory by measurements with the interferometer, but even in this case serious difficulties might arise if the intensity distribution curve were not of some simple form. In a recent investigation KING and KOCH* have described a method of investigating the structure of spectrum lines. The method adopted by these investigators consists in photographing the spectrum under a high dispersion, and in obtaining a curve relating the density of the image on the photographic plate to the wave-length. This is accomplished by causing the plate to move slowly in front of a slit through which light from a constant source is passed, and by continuously recording the resulting changes in the intensity of this light by a method involving the use of the photo-electric cell. The method has yielded valuable results in the study of the variation in the character of spectrum lines under different conditions of excitation, but it would appear difficult to employ a method of this kind to determine the quantitative intensity distribution in the lines on account of the eccentric and somewhat anomalous relations which determine the form and density of photographic images. In adopting a photographic method for quantitative investigation the following phenomena have to be taken into account :—

(I.) There is no linear relation, and indeed no very definite relation, between the density of the image on a photographic plate and either the intensity of the light which produces the image or the duration of the exposure. The relation varies with different brands of plate and is affected by the chemical treatment of the plate in developing the image. An extreme case occurs when the image becomes solarized, or over-exposed to such a degree that it is no longer capable of development, a phenomenon well known to spectroscopists as the cause of the spurious reversal of spectrum lines.

(II.) The product of the intensity of the light by the time of exposure does not produce a constant value of the density of the photographic image, that is to say, a

* 'Astrophys. Journ.,' 39, p. 213, 1914.

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different density is obtained by doubling the intensity of the light and halving the time of exposure.

(III.) The sensibility of the photographic plate varies for different wave-lengths. This, of course, depends on the particular kind of plate used, but may be neglected in the investigation of broadened emission lines, since the sensibility of the plate may be taken as constant over the short range of wave-length covered.

(IV.) Irradiation, or spreading of the image on the photographic plate, which has recently been the subject of a quantitative investigation by TUGMAN.* Owing to the scattering of light by the grain of the plate the size of a photographic image increases with the time of exposure or the intensity of the light.

It is therefore evident that if quantitative measurements are to be made by a photographic method, the method adopted must comply with the principle,† that two sources of light or two regions of illumination can only be considered to be of equal intensity when they produce the same degree of density in the same time on portions of the same photographic plate. It is believed that the method adopted in the present investigation fulfils these conditions and is independent of the eccentricities of the photographic plate.

An accurate wedge of neutral-tinted glass, cemented to a similar wedge of clear glass so as to form a plane parallel plate, was mounted immediately in front of the slit of a spectroscope, in the manner commonly used for determining the sensibility curves of photographic plates. Under these conditions the spectrum of a discontinuous source thrown on to the slit through the neutral wedge is seen to consist of lines which are bright at one end, corresponding to the thin end of the wedge, and gradually fade off towards the region corresponding to the thick end of the wedge. The apparent length of a line depends on its intensity, and the relative intensity of two adjacent lines can be determined by measuring the lengths at which they can just be seen. Since in broadened spectrum lines the intensity, generally speaking, falls off more or less regularly from the maximum of intensity, a broadened line appears, with the arrangement described, as a wedge, the apex of which corresponds to the point of maximum intensity. By a measurement of the shape of the photographed image of such a wedge, it is possible to calculate the distribution of intensity in the broadened line. It is only necessary to pick out points of any convenient density which can be recognised, and to measure their height from the base of the wedge. The method therefore conforms with the conditions that have been laid down, and is independent of the eccentricities of the particular plate used or its subsequent treatment. Since the density which can be most easily recognised is small, it is evident that the results will not be vitiated by irradiation provided that the spreading due to irradiation from the centre of the base of the wedge is small in comparison

* 'Astrophys. Journ.,' 42, p. 331, 1915.

† *Cf.* HOUSTOUN, 'Roy. Soc. Edinburgh Proc.,' 31, p. 521, 1911.

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with the total width of the base. It is therefore necessary that the dispersion of the spectroscope should be sufficiently great in relation to the width of the lines. In the present investigation the lines measured have been of such a breadth that this condition is amply fulfilled, and, moreover, the photographs show that this is the case. At the maximum in the base of the wedge the image is spread out. If, however, the dispersion of the spectroscope is sufficiently great this spreading is no longer visible at the edges of the base of the wedge. An exaggerated drawing of the effect of irradiation on the wedges is shown in fig. 1. In "A" the effect of irradiation is seen at S, but at P and Q, which represent the boundary of the wedge and the "recognisable density," the effect is no longer visible. In "B" it is evident that the

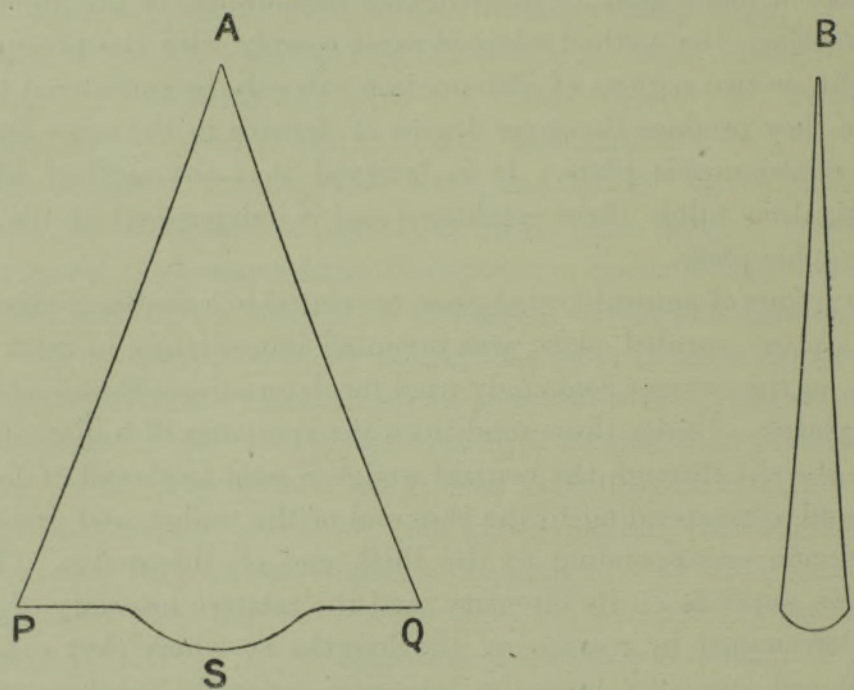

Fig. 1.

effect of irradiation is not eliminated, and that a higher dispersion must be employed if reliable measurements are to be made for the line in question.

(IV.) *Experimental.*

For the production of the spectra investigated condensed discharges were employed from an induction coil capable of giving a ten-inch spark in air, and in parallel with a condenser having a capacity of 0·0025 microfarad. In the case of hydrogen the condensed discharges were passed between aluminium or platinum points in a glass vessel containing hydrogen at atmospheric pressure. In the case of helium a vacuum tube containing the gas at a pressure estimated at somewhat above a millimetre of mercury was employed, and in this case a spark gap was put into the circuit. The

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spectrum lines produced under these conditions are of such a breadth that the dispersion of a single prism spectrograph was found to be sufficient. The spectrograph consisted of a large model constant deviation spectroscope by Hilger with a camera attachment. The neutral wedge, which was supplied by the same firm, was fastened on to a diaphragm which was fitted in grooves immediately in front of the slit. The slit width used was 0·025 mm. The width of the slit might necessitate a correction in the interpretation of the photographs, but since in the present case the greatest correction would be less than one per cent. of the width of the base of the wedge, it may for the present purpose be neglected. The curvature of the spectrum lines obtained with prism spectrographs has also been considered as a possible source of error, but this also was found to be negligible over the length of slit in use.

The greatest care was taken to ensure the even illumination of the slit, since this might give rise to serious errors. In the case of vacuum tubes there is no difficulty in ensuring this, and in every case the even illumination of the slit was verified before the wedge was put into position. In the case of the spark discharges through hydrogen at atmospheric pressure, the light was concentrated on to the slit by means of a sphero-cylindrical condenser, and in some cases a piece of ground glass was interposed as a further precaution. WRATTEN and WAINWRIGHT'S panchromatic were used, and were in some cases intensified with mercuric bromide and sodium sulphide after fixing. Enlargements were then made on to bromide paper with an enlarging apparatus provided with a Zeiss-Tessar lens, which gives no appreciable distortion over the field required. Since, however, it is in general more easy to work with a negative than a positive, the enlargements were usually carried out in two stages, the first enlargement being made on a Wratten "process" plate or a Paget "half-tone" plate, and the second enlargement on bromide paper.

There remains the personal error in picking out the points of equal density. It is believed that this has been almost entirely eliminated by enlarging the plates through a ruled process screen, the resulting image thus consisting of fine black dots on a white ground. In this way measurements may be easily made by pricking out the last dot visible at a large number of points on the wedge, and subsequently drawing a curve through these points. The extreme dot visible is a very definite point and the drawing of the curves is thus reduced to an almost mechanical process, whereas the recognition of points of equal density on photographs, which have not been prepared in this way, is a matter requiring considerable practice and would undoubtedly be a source of error.

For investigations of a more qualitative nature of the spectrum of lithium, a concave grating spectrograph was used. This instrument consisted of a concave grating of four feet radius of curvature and 20,000 lines to the inch and was mounted according to the arrangement described by EAGLE,* the dispersion being about 10 Å.U per millimetre.

* 'Astrophys. Journ.,' 31, p. 120, 1910

(V.) *Theoretical Discussion.*

We may now consider the mathematical interpretation and analysis of the curves obtained.

1. A critical intensity of illumination I_c must exist, such that any intensity smaller than I_c, falling on the plate under the conditions of, and for the time occupied by the exposure, does not produce an effect which can be perceived by the eye. More generally, it would be equally convenient for many purposes to define I_c as the intensity which will produce any specified amount of blackening on the plate, and in the method adopted the amount of blackening specified will represent a dot which is just visible on the enlarged photograph. For, as will appear later, the *loci* of all the points of equal blackening on the plate, due to one component, form similar curves, which only differ in regard to the values of the constants contained in their equations. In determining the general nature of the curve given by any line—and therefore the law of energy distribution in the original image of the slit without incidence on the wedge—this more general conception of I_c is sufficient.

It has been pointed out that the type of broadening of a spectrum line from a gas at low pressure and excited by uncondensed discharges is in accord with discussions based on the theory of probability, following the law

$$I = I_0 e^{-k^2x^2},$$

where I_0 is the intensity at the "centre" of the line—only the case of symmetrical broadening is at present contemplated—and I the intensity at a distance x from the "centre," measured on the wave-length scale, and k a constant.

The assumption has usually been made hitherto that the broadening associated with the condensed discharge also followed the probability law, although the actual amount of broadening is of another order of magnitude under suitable conditions. In fact any other supposition raises difficulties in the physical interpretation according to any suggestions yet put forward. It has never been implied that the effect may not be complex, and due to the joint action of several causes. The broadened line might therefore be formed by the superposition of several probability curves—one arising from each cause—and the resultant intensity law might then cease to be of the usual type, although that type pertained to each of its components. Cases of unsymmetrical broadening can also come into the scope of such a view.

Perhaps the most fundamental result which emerges from a preliminary inspection of the plates is the necessity of abandoning this view. The plates contain photographic records of the intensity curves—showing variation of intensity with wave-length—across certain lines, and although the traces on the plates are not the actual intensity curves, which may be derived from them by a simple formula, yet abrupt changes of curvature in the intensity curves must be accompanied by similar changes on the plates. In other words, the number of separate components, whatever their origin,

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in a broadened line is represented on the photographic plate, after passage through the wedge, by an equal number of "kinks" in the bounding curve of the darkened patch, provided, of course, that the separations exceed certain limits. A smooth curve, containing no abrupt change of curvature—shown, for example, very definitely in the upper part of the plates for the line H_α (Plate 2)—indicates either a regular law of intensity in the corresponding portion of the original spectral line, or a number of components of very small separation. If in passing across the line, on the wave-length scale, a place was reached where, through the presence of a new and sufficiently separated component, a definitely new law of intensity appeared, a kink would be found on the final plate in the corresponding position. No such kink occurs in the upper portion of the H_α curve, which therefore presents us with one of these alternatives. A first inspection indicates that, for some value of n, $y^n = Ax$ should be a good approximation to the shape of this curve, where A is positive, the axis of x being that of the curve and the origin being at the vertex.

The curvature is away from the axis of x, so that dy/dx increases with x, and d^2y/dx^2 is positive. Thus *n is less than unity.* The curve is, in fact, not unlike the two branches of a semi-cubical parabola, in which $n = \frac{2}{3}$. This property of curvature away from the axis is general throughout the plates, as a casual inspection shows, in all regions where the curvature appears fairly continuous, and therefore determined by only one or by several very close components in the primary broadened line. A single component must therefore ultimately produce, after passage through the wedge, a curve whose equation is at least approximately of the form

$$y^n \propto x,$$

where n is less than unity.

Consider now the curve to be expected for a component satisfying the probability law of intensity.

$$I = I_0 e^{-k^2x^2},$$

where I_0 is the intensity of its centre, and x is the distance of the intensity I from the centre. The wedge diminishes intensity in an exponential manner, and can be defined by a constant ρ such that, if an intensity I_1 falls on the wedge, traverses a thickness η, and emerges as an intensity I_2, $I_2/I_1 = e^{-\rho\eta}$. The intensity I is diminished to I_c, the critical intensity already defined, by a thickness η of wedge given by

$$I_c = Ie^{-\rho\eta} = I_0 e^{-k^2x^2-\rho\eta}.$$

In the figure (fig. 2) ABCD represents the lower surface of the wedge, AB being the intersection of the upper and lower faces, where the thickness diminishes to zero. The shaded area on the lower face of the wedge denotes the final record of the broadened line, whose plane was originally parallel to the lower face and above the upper. Around the boundary of this shaded area the intensity is everywhere I_c,

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through the combined action of the exponentials of arguments $-k^2x^2$ and $-\rho\eta$ respectively. At X and Y, for example, $\eta = 0$, since no wedge has been traversed, and therefore, if $XY = 2D$,

$$I_c = I_0 e^{-k^2D^2}.$$

In fact, X and Y are the traces of the extreme ends (photographically extreme) of the original line, and 2D would be its photographic breadth in the absence of the wedge.

At the apex Z of the shaded area, on the contrary, $x = 0$, for it corresponds to a point on the central axis of the original line. If therefore H is the height of the curve,

$$I_c = I_0 e^{-\rho H \tan \alpha},$$

where α is the angle of the wedge, for $\eta = H \tan \alpha$ for the point Z. If y is the distance of any other point P, on the boundary of the area, from the line AB, and x

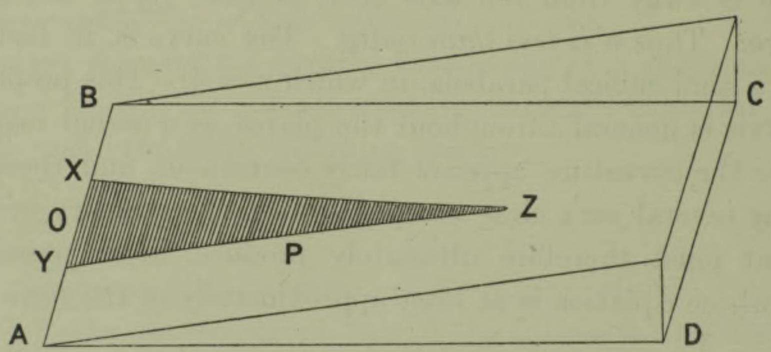

Fig. 2.

its distance from the axis OZ of the curve, then x is also the distance from the centre in the original line, of the light affecting P, and $y \tan \alpha$ is the thickness of wedge it has passed through, so that if (x, y) are the co-ordinates of P, referred to an origin at the intersection of base and axis,

$$I_c = I_0 e^{-k^2x^2 - \rho y \tan \alpha},$$

$$= I_0 e^{-k^2D^2} = I_0 e^{-\rho H \tan \alpha},$$

or

$$k^2x^2 + \rho y \tan \alpha = k^2D^2 = \rho H \tan \alpha,$$

whence, eliminating k^2,

$$Hx^2 + D^2(y - H) = 0,$$

and the curve on the plate should be parabolic. An obvious change of axes reduces this to

$$y^2/x = D^2/H.$$

But we have already seen that, if the curve is $y^n \propto x$ with this choice of axes, n is less than unity from all the plates. We must conclude that the law of intensity for a single component, or a set of close components, broadened by the condensed discharge, is not a probability law. Whatever it may be, it must be far removed from this, for the curvature of every curve on the plates is diametrically opposite to the requirements of the law. We are therefore not dealing with a case in which the law ceases to be a good approximation, but with something fundamentally different. It is evident that broadening due to a condensed discharge has no relation to the ordinary phenomena, and that the uses made of these phenomena, for example, by BUISSON and FABRY, are definitely inapplicable if the conditions of excitation are those of a condensed discharge. This definite conclusion serves to remove several anomalies which have arisen in connection with the application of interference methods to spectral lines, but which need not be classified in detail here.

In view of this failure of the ordinary superposed probability curves towards an explanation of the laws of intensity found in these experiments, it is necessary, before proceeding to a detailed examination of the plates, to give the general theory of the experiment, which from a mathematical point of view is simple. With the notation selected above, let I_0 be the intensity on the axis of a spectral line, and let the law of variation from the axis be $f(x)$. Then the intensity at a distance x along the wave-length scale is $I_0 f(x)/f(0)$. For example, in the preceding case $f(x) = e^{-k^2x^2}$ and $f(0) = 1$. A depth η of wedge reduces this to $I_0 f(x) e^{-\rho\eta}/f(0)$.

If H is the height and 2D the breadth of the resulting image on the plate,

$$I_c = I_0 f(D)/f(0) = I_0 e^{-\rho H \tan\alpha}$$
$$= I_0 f(x) e^{-\rho y \tan\alpha}/f(0)$$

and

$$f(x)/f(D) = e^{\rho y \tan\alpha}.$$

Using a function $\psi(x)$ instead, where $f(x) = e^{-\psi(x)}$, as being more convenient for calculations, equally general, and more suited to the physical necessity for an exponential type of law

$$\psi(D) - \psi(0) = \rho H \tan\alpha = \psi(x) - \psi(0) + \rho y \tan\alpha.$$

Referring the curve to new axes at its vertex, as in the case already discussed, transferring the origin through a distance H, reversing the axis of y, and finally, interchanging the axes of x and y, we obtain

$$\psi(y) = \rho x \tan\alpha,$$

and the law of intensity denoted by ψ can be found if the equation of the curve on the plate is determined. For example, if the photograph has the equation

$$y^n/x = \text{constant}.$$

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where n is a definite number, $\psi(y) \propto y^n$, and $f(x) = e^{-\psi(x)} = e^{-qx^n}$, where q is constant. The law of intensity in the original line is therefore

$$I = I_0 e^{-qx^n},$$

being the probability curve when the final curve is a parabola. A case of obvious interest is that of an ordinary exponential distribution of intensity

$$I = I_0 e^{-qx},$$

where q is constant, in the original line. The equation to the photograph would then be

$$qy = \rho x \tan \alpha,$$

so that it becomes a straight line, from which the value of q could be measured at once when the optical properties of the wedge, defining ρ and α, are known. This equation, of course, like those preceding, applies to one side of the photograph only, the other side being the optical image of the first in the axis of the photograph. For example, the present case would present, as the complete boundary, two straight lines intersecting at the apex of the curve, and inclined at an angle closely given by $2\rho\alpha/q$, where α is the small angle of the wedge.

If the law were partly exponential and partly of the probability type, or $I = I_0 \exp(-k^2x^2 - qx)$, where k^2 and q are *positive* constants, the graph on the plate would become

$$k^2y^2 + qy = \rho x \tan \alpha,$$

and it is easily demonstrated that this is a parabola exactly similar—and, in fact, equal—to the parabola obtained when $q = 0$, but shifted on the plate so that its axis has moved parallel to itself. The curve is therefore still symmetrical about its axis and curved *towards* it, so that this mixed law is incapable of explaining the characteristics of the photographs even on general grounds. In fact, the constant q has no influence on the radius of curvature. It would, however, have an influence if the law with which the simple exponential is combined were anything other than the law of probability.

This lack of influence of q, however, only applies to corresponding points, and in order to avoid misconception, a more complete account is necessary, for the curve as seen on the plate would actually appear flatter and be of smaller extent. At the same time it undergoes a sudden change of curvature at the vertex. In the annexed figure (fig. 3) the dotted curve is the parabola which would be obtained when $q = 0$. The other parabola ABCDE is the shifted parabola obtained when q is not zero, as explained already. But only the portion ABC appears on the pláte, for the axis OX cannot be disturbed by the presence of the new exponential factor, which must also lessen the height of the curve to the value CX. What is actually seen is ABC and its image in OX, or the shaded area in the figure bounded by two arcs

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of parabolas whose vertices are not at C, which therefore exhibits a sharp peak. In fact, the original dotted parabola really consists of arcs of two parabolas which happen to be coincident when $q = 0$, and the analysis always applies only to one side of the axis, as was emphasised earlier.

The interaction of two laws of energy distribution in a line, one being the simple exponential law, could therefore explain the peaked appearance at the vertices of the photographs, but it is incapable of explaining the nature of the curvature if the other law is that of probability. It is evident on inspection of corresponding points why one curve is flatter than the other, although the parabolas are equal.

On the supposition that H_α is not complex in these experiments (a supposition which is ultimately disproved), it is a matter of practical importance to isolate the

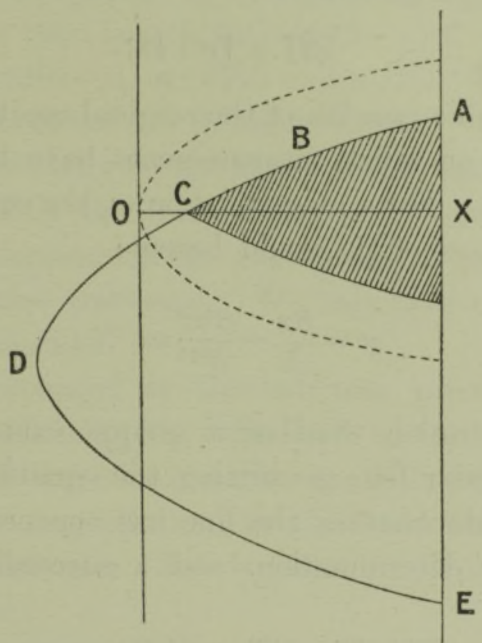

Fig. 3.

simple exponential law which may be superposed on any other, and although the curves appear, in their continuous parts, to follow a law of the form $y^n \propto x$, we must assume, in view of their peaked nature, that the best representation in terms of one component will be

$$y^n + \delta y = \beta x,$$

where δ and β are constants, n being less than unity. The curves, when of continuous curvature, are obviously so nearly straight lines—as, for example, in the upper part of the curves for H_α—that the simple exponential law is evidently the predominant feature, and much analysis is thereby saved. For, as a first approximation, $y = \beta x/\delta$, and the second approximation is easily found to be

$$y = \frac{\beta x}{\delta} - \frac{\beta^n x^n}{\delta^{n+1}}.$$

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The relation of these constants δ and β to the constants of the energy distribution of the original spectral line may be found as follows:—If the law of intensity distribution is

$$I = I_0 e^{-kx^n - qx},$$

around the maximum at $x = 0$, and if H and 2D are the height and breadth of the photograph,

$$\rho y \tan \alpha + kx^n + qx = kD^n + qD = \rho H \tan \alpha$$

with reference to the old axes. Taking the new axes at the vertex,

$$ky^n + qy = \rho x \tan \alpha.$$

Thus

$$\delta = q/k, \quad \beta = \rho \tan \alpha/k$$

and also

$$BH = D^n + D\delta$$

where 2D is the photographic breadth of the original spectral line.

The actual photographs on which measurements have been made were previously magnified in definite ratios. For a magnification m, the equation of the upper portion of such a photograph as those of H_α would become

$$y = \frac{\beta x}{\delta} - \frac{\beta^n x^n}{\delta^{n+1}} m^{1-n}.$$

It is necessary to determine whether a unique value of n exists through the photographs of one particular line, permitting the equations of the contours to take this form, in order to decide whether the line has one or more components. H_α is a suitable medium for this determination, and a succeeding section takes up this question.

(VI.) *The Effect of Dispersion.*

When the photographs are magnified on a large scale they all appear unsymmetrically broadened towards the violet. This is the effect to be expected from the fact that the spectrum produced by the prism is not normal, and it is necessary, before a detailed analysis of the photographs can be made, to calculate the asymmetry due to this cause and to compare it with the actual effect observed. A complete account of this problem is given below in connection with the best magnified photograph obtained for H_α. The dispersion on the original plate, before magnification, was known to be given very accurately by the formula

$$\lambda = \lambda_0 + C/(n+n_0)$$

where $\lambda_0 = 2257{\cdot}5$, $C = 116{,}802{\cdot}9$, λ is in Å.U., and $n+n_0$ is in millimetres of the scale. The scale reading for the centre of the pattern of $H\alpha$, $\lambda = 6563$, is, therefore, on the original plate

$$n+n_0 = 116{,}802{\cdot}9/(6563-2257{\cdot}5) = 27{\cdot}13 \text{ mm.}$$

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We shall suppose provisionally that the law of energy distribution round the central component of the original line is the same on both sides, so that with equality of dispersion, the final pattern would be symmetrical. Let $6563 \pm \alpha$ be the limiting wave-lengths which can just be seen on this pattern at the thin end of the wedge. Then the corresponding scale readings at the ends of the pattern are

$$n + n_0 = C/(6563 - \lambda_0 \pm \alpha),$$

or

$$27{\cdot}13 \mp C\alpha\,(6563-\lambda_0)^{-2} + C\alpha^2\,(6563-\lambda_0)^{-3}.$$

The length of the red end of the pattern is $\alpha C\,(6563-\lambda_0)^{-2} - \alpha^2 C\,(6563-\lambda_0)^{-3}$ and of the violet end, $\alpha C\,(6563-\lambda_0)^{-2} + \alpha^2 C\,(6563-\lambda_0)^{-3}$, neglecting higher powers. The difference is $2\alpha^2 C\,(6563-\lambda_0)^{-3}$ and the total length $2\alpha C\,(6563-\lambda_0)^{-2}$. If this total length is d, the difference becomes $\alpha d/(6563-\lambda_0)$ or $(6563-\lambda_0)\,d^2/2C$. By calculation, this becomes $d^2/54{\cdot}26$ in the present case, where d is in millimetres.

This calculation is valid not only for the extreme thin end of the wedge, but for any thickness of wedge, for both the wave-lengths, $6563 \pm \alpha$, have the same original intensity, and therefore disappear on the photograph at equal heights, corresponding to equal thicknesses of wedge traversed. We may now apply this result to one of the photographs of H_α (Plate 2).*

This plate has been reproduced by the half-tone process, which reproduces the dotted effect used in determining the boundary of the curve. The vertex of the curve* is well defined, and the axis must be parallel to the original slit, and can be determined precisely. The magnification in this case was $\times 33$, and the breadth of the curve at its base is 59·0 mm. The breadth of the original plate was therefore $59/33 = 1{\cdot}7879$ mm. Thus,

$$d = 1{\cdot}7879 \text{ mm.} = v + r$$

where v and r are the breadths of the violet and red ends.

Also

$$v - r = d^2/54{\cdot}26 = 0{\cdot}0589 \text{ mm.}$$

The difference on the photograph magnified 33 times is $0{\cdot}0589 \times 33$ or 1·97 mm., but where, on this photograph, $d = 14$ mm. say, the difference is 1·97/16 or 0·12 mm. and could hardly be observed. Even the magnified curves must therefore look very symmetrical at some distance from the apex, and this is actually the case. An important corollary from this result is that the upper part of the curve can be used to give a geometrical construction for the determination of the axis of the curve. This method has been applied to H_α, to check the supposed position of its axis, with

* In the reproduction (Plate 2) the whole of the paper is dotted, and the outline cannot therefore be traced exactly. In the original photographs used for measurement, the only dots visible are those which build up the magnified image, thus enabling the boundary to be precisely determined.

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very accurate agreement. When the axis was thus verified, measurements of the breadth between the two extreme dots visible laterally were taken at various levels on the height of the curve. It is not thought necessary to give these measurements in detail, and perhaps one example will suffice. The measured distance between the extreme dots at the lower end of the photograph, where it is broadest, is 59·0 mm. as stated already, and the violet and red portions have breadths 30·5 and 28·5, measuring on either side of the axis. This difference is 2·0 mm. against the theoretical value 1·97. This agreement, typical of the agreement throughout, is a convincing proof that the broadened H_a is, in its energy distribution, *absolutely symmetrical* about its centre, and that the apparent asymmetry—only evident to the eye on the magnified photographs—is entirely due to the fact that the prismatic spectrum is not normal.

This is the second fundamental result of the work—that *the broadening of* H_a *under the condensed discharge is an absolutely symmetrical one.*

To a high order of approximation, inequality of dispersion lengthens the breadth of the violet and shortens that of the red to an equal extent, so that their sum is the breadth of the curve with a dispersion uniformly equal to that at λ6563. To draw a graph of the symmetrical curve for uniform dispersion, therefore, we merely require to measure the total breadth of the photograph for various heights, and plotting half total breadth against height, we obtain one side of the curve for uniform dispersion. Now the total height, from base to apex, of the H_a curve in question, is 192 mm., and the excess of breadth of the violet over the red end, even at the base, is only 2 mm. in a total breadth of 59 mm. The alteration in shape caused by this correction is therefore very slight, and can produce no appreciable tendency to a parabolic form on either side. The previous conclusion as to the absence of a probability law remains, therefore, unaffected.

(VII.) *The Complex Structure of* H_a *when Excited by Condensed Discharges.*

The symmetry of H_a being established, the two alternatives still remain. H_a may be a single component symmetrically broadened—to disprove this supposition is our immediate object—or a set of symmetrically-arranged but close components, each broadened in a symmetrical manner. The theory of this second case has not yet been given, and in assuming that it is a possible interpretation of the photographs, we are anticipating the theory given later. Confining attention for the present to the first alternative, and recalling that any law must, for physical reasons in the case of emission, be of some exponential type, and from the appearance of the curves, mainly a linear exponential, we have the formula, for magnification m,

$$y = \frac{\beta x}{\delta} - \frac{\beta^n x^n}{\delta^{n+1}} m^{1-n},$$

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n being less than unity, and δ large and positive. The first condition, as regards n, is necessary to secure the curvature in the right direction. Now this could also be secured mathematically if n were greater than unity, and δ negative, but this case is a physical absurdity, for it signifies a law of intensity in the original light of the form

$$I = I_0 e^{-a^2x+b^2x^n},$$

where a and b are real constants, and $n > 1$. The intensity would then begin by decreasing from the centre, and finally *increasing* without limit. This is contrary to experience and also to physical possibility. But it is unfortunately the case to which we are led when an attempt is made to apply the formula to the curve for H_α. The following numerical example from one photograph makes this clear, and indicates at the same time that small changes in the measurements would not reverse the conclusion.

β/δ at the vertex may be obtained with accuracy as the initial slope, and is found to be 0·0573, by a construction involving the result as a ratio of two large distances. The following points are on the curve, and distances are expressed in millimetres.

$$\left.\begin{array}{l} x = 162{\cdot}5 \\ y = 16{\cdot}0 \end{array}\right\}, \qquad \left.\begin{array}{l} x = 192{\cdot}0 \\ y = 29{\cdot}5 \end{array}\right\},$$

and applying the formula we find,

$$n = 5{\cdot}97, \qquad \delta/m^{n-1} = -0{\cdot}870.$$

The mixed law,

$$I = I_0\, e^{-qx-kx^n},$$

can therefore give no interpretation of the curves, and a more general conclusion is possible. For the result may be extended in the same way to a law compounded of three, when further measurements are made. It is not thought necessary to reproduce the calculations to this effect. The conclusion, therefore, appears inevitable that the details of the shape, and even the general form, of the curve H_α, are not compatible with the view that H_α contains only one component broadened, perhaps by various agencies, simultaneously by any physically possible exponential laws, the total argument of the exponential being *additive* in the complete law. We are compelled to seek an explanation of the curve in terms of several components whose individual curves are superposed, and are led directly to the Stark effect as the foundation of the whole phenomenon. Several qualitative reasons have already been advanced in favour of this hypothesis, and it now appears further that a quantitative study of the curves necessitates the same hypothesis. For if several components are to be admitted, only the Stark effect seems capable of providing them, and the fact that they must be symmetrical in H_α enhances this conclusion. The components are conspicuous in $H\beta$

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and some other cases, but in H_α a closer scrutiny is required to reveal them. In order to cover such cases the theoretical discussion has been made somewhat complete.

(VIII.) *General Theory of a Symmetrically Compound Line.*

If H_α has close components, the law of attenuation of each component from its maximum is now certainly that of the simple exponential,

$$I = I_0 e^{-qx},$$

for the whole of the curve for H_α is very close to a straight line, and for nearly half its length is almost entirely straight. Afterwards it broadens convex to its axis, but not rapidly, and although so irregularly as to invalidate attempts to interpret it by a single exponential of any possible argument, the curvature is nevertheless at *every*

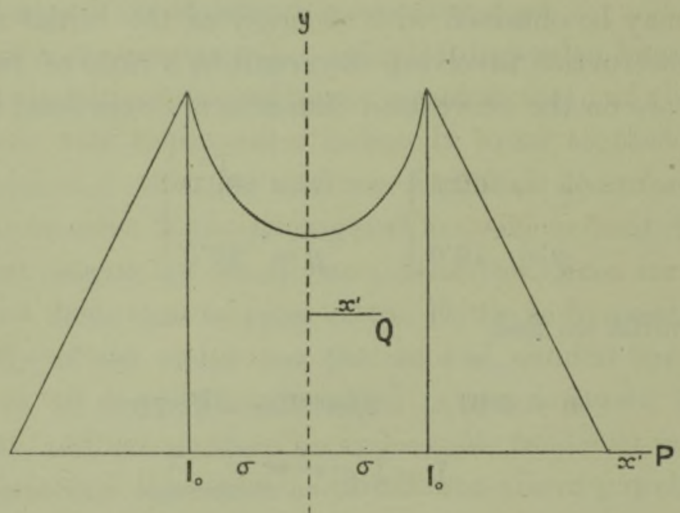

Fig. 4.

point away from the axis. Several close components with somewhat different rates of attenuation, but with axes nearly coincident, are at once suggested, and will be shown to provide a complete explanation of these peculiarities. No other exponential arrangement appears capable of doing so.

As the components of H_α are symmetrically arranged, we consider first the effect of a pair of equal components separated by an interval 2σ.

Let I_0 (fig. 4) be the axial intensity of either. A dotted line in the figure is midway between their axes, and is taken as the axis of y. Then at a point P of co-ordinate x outside both axes the intensity is $I = I_0 e^{-q(x-\sigma)} + I_0 e^{-q(x+\sigma)} = 2I_0 \cosh q\sigma e^{-qx}$ and this would be produced by a *single* line of axial intensity $2I_0 \cosh q\sigma$ midway between. But at a point Q (x') between the axes the intensity is

$$I = I_0 e^{-q(\sigma+x')} + I_0 e^{-q(\sigma-x')} = 2I_0 e^{-q\sigma} \cosh qx',$$

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following a different law. A wedge whose length lies along y would produce a curve of critical intensity I_c which, outside both axes, would have an equation

$$I_c = 2I_0 \cosh q\sigma e^{-qx-\rho y \tan\alpha}$$

or

$$\rho y \tan\alpha + qx = \log_e (2I_0 \cosh q\sigma / I_c)$$

and be straight. But between the axes the equation is

$$I_c = 2I_0 \cosh qx \,.\, e^{-q\sigma-\rho y \tan\alpha}$$

or

$$\rho y \tan\alpha = \log_e (2I_0/I_c) - q\sigma + \log_e \cosh qx,$$

which is curved. We can verify at once from these equations that dy/dx is discontinuous and changes sign when $x = \sigma$, and that the form of the curve of intensity I_c is as shown in the figure (fig. 4). The summits of these curves, however, are not the summits which the separate components would individually show. The upper parts of the photographs of H_β indicate this appearance very precisely, so that the strongest components of H_β form a symmetrical pair.

Before proceeding to the effect of superposition of such pairs, together with a possible central component, we must prove a very general theorem. The main characteristic of all the curves which have been photographed, not only of hydrogen lines, but of helium and lithium, is that they contain no point at which the curvature is towards the axis. In other words, if y is measured as in the last figure, d^2y/dx^2 is always positive whatever the sign of dy/dx. Apparently the only exponential arrangement which is physically possible and possesses this property in general is the class of curves dealt with in the theorem. A proof of this statement would occupy some space, and we therefore merely prove that this class has the necessary property.

Consider a set of lines, n in number, with any rates of attenuation $q_1, q_2, \ldots, q_n$, whose axes are coincident. Their central intensities are $I_1, I_2, \ldots, I_n$. If $\kappa = \rho \tan\alpha$, the bounding curve of the photograph they produce is given by the equation

$$I_c e^{ky} = \sum_{r=1}^{r=n} I_r e^{-xq_r},$$

when they are all simply exponential. Accordingly, by differentiating twice,

$$\kappa I_c \frac{dy}{dx} e^{ky} = -\sum_1^n I_r q_r e^{-xq_r},$$

$$\kappa^2 I_c \left\{\left(\frac{dy}{dx}\right)^2 + \frac{1}{\kappa}\frac{d^2y}{dx^2}\right\} e^{ky} = \sum_1^n I_r q_r^2 e^{-xq_r},$$

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whence, by eliminating dy/dx and e^{ky}, we derive

$$\sum_1^n \mathrm{I}_r e^{-xq_r} \cdot \sum_1^n \mathrm{I}_r q_r^2 e^{-xq_r} - \left(\sum_1^n \mathrm{I}_r q_r e^{-xq_r}\right)^2 = \kappa \frac{d^2y}{dx^2}\left(\sum_1^n \mathrm{I}_r q_r e^{-xq_r}\right)^2.$$

Let $\lambda_r = \mathrm{I}_r e^{-xq_r}$, so that $\lambda_1, \lambda_2, \ldots, \lambda_n$ are all necessarily positive by physical considerations. Then the sign of d^2y/dx^2 is that of

$$\sum_1^n \lambda_r \cdot \sum_1^n \lambda_r q_r^2 - \left(\sum_1^n \lambda_r q_r\right)^2 = \sum_{r=1}^{r=n} \sum_{s=1}^{s=n} \lambda_r \lambda_s (q_r - q_s)^2.$$

This is a sum of squares with positive coefficients, and is essentially positive for all values of x. Thus d^2y/dx^2 is always positive. Even if some of the quantities q_r were positive, this proof would be equally valid, and curves of equal density on the photograph would have d^2y/dx^2 positive at all points.

The curves obtained with any of STARK'S resolutions, if the components followed the simple exponential law, would all be included in this class. For they involve a possible central component $\mathrm{I}_0 e^{-qx}$ and pairs of components. A pair at points on the same side of both axes, if of separation 2σ, produces an intensity $2\mathrm{I} \cosh q\sigma e^{-qx}$ at a point x, where $2\mathrm{I} \cosh q\sigma$ is constant. At a point x between the axes the intensity is $\mathrm{I}e^{-q\sigma}(e^{qx}+e^{-qx})$, and the pair is equivalent to two central components, one increasing and the other decreasing. Any Stark resolution is therefore, under this law, equivalent to a set of components whose axes coincide, and the theorem follows.

As already stated, this is the only possible exponential arrangement with the property in question, and this theorem in itself provides a very convincing argument in favour of the suggested theory of broadening, even when a close scrutiny is required to reveal the components.

Let now a central component be superposed on a symmetrical doublet of separation 2σ. If the suffixes 1 and 2 refer to the component and the doublet, the curve of intensity I_c is, between $x = 0$ and $x = \sigma$,

$$\mathrm{I}_c e^{py \tan a} = \mathrm{I}_1 e^{-q_1 x} + 2\mathrm{I}_2 e^{-q_2\sigma} \cosh xq_2$$

and, between $x = \sigma$ and $x = \infty$,

$$\mathrm{I}_c e^{py \tan a} = \mathrm{I}_1 e^{-q_1 x} + 2\mathrm{I}_2 e^{-q_2 x} \cosh \sigma q_2.$$

The two branches meet at $x = \sigma$, and the ratio of the two values of dy/dx at $x = \sigma$ is

$$\left\{1 - \frac{2q_2\mathrm{I}_2}{q_1\mathrm{I}_1} \sinh \sigma q_2 \cdot e^{-\sigma(q_2-q_1)}\right\} \Big/ \left\{1 + \frac{2q_2\mathrm{I}_2}{q_1\mathrm{I}_1} \cosh \sigma q_2 \cdot e^{-\sigma(q_2-q_1)}\right\},$$

which is obviously less than unity. It can be negative if I_2 is sufficiently large compared with I_1, and then the curve would have a sharp peak at $x = \sigma$. Otherwise

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there is only a discontinuity in the slope of the form shown in the figure (fig. 5), the dotted lines being parallel to x and y.

If $q_1 = q_2$, the lower branch is straight.

We may pass at once to the general case of a central component and n doublets

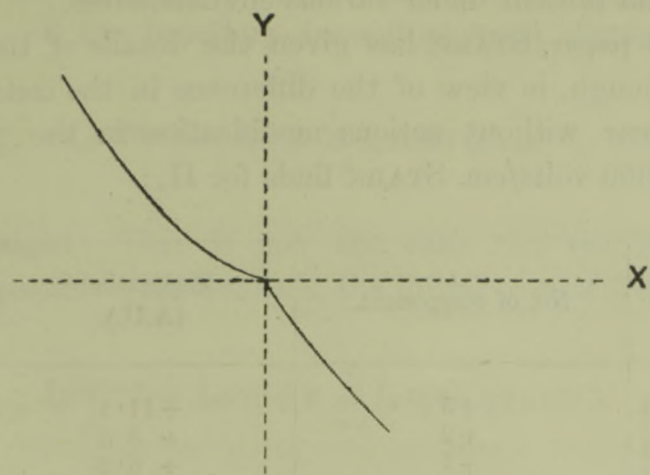

Fig. 5.

symmetrically arranged round it. Between the centre and $x = \sigma_1$, an axis of the first doublet, the intensity curve I_c becomes

$$I_c e^{py \tan\alpha} = I_0 e^{-xq_0} + \sum_1^n 2I_r \cosh xq_r \cdot e^{-q_r\sigma_r}.$$

Between this axis and one of the second doublet at $x = \sigma_2$,

$$I_c e^{py \tan\alpha} = I_0 e^{-xq_0} + 2I_1 \cosh q_1\sigma_1 \cdot e^{-xq_1} + \sum_2^n 2I_r \cosh xq_r \cdot e^{-q_r\sigma_r}.$$

Between $x = \sigma_2$ and $x = \sigma_3$, relating to the third doublet,

$$I_c e^{py \tan\alpha} = I_0 e^{-xq_0} + 2I_1 \cosh q_1\sigma_I \cdot e^{-xq_1} + 2I_2 \cosh q_2\sigma_2 \cdot e^{-xq_2} + \sum_3^\infty 2I_r \cosh xq_r \cdot e^{-q_r\sigma_r},$$

and so on. In any special case, the branches of the curve may be studied from these equations. The whole curve has discontinuities in dy/dx at $x = \sigma_1, \sigma_2, \ldots, \sigma_n$, and these may be of the form shown above, or actual peaks, such as can be seen in the photographs of H_β which have been taken by this method. Much depends on the relative values of the quantities q for the various components. When a peak occurs, say at $x = \sigma_r$, it is easy to calculate the lowest depth of the curve between $x = \sigma_{r-1}$ and $x = \sigma_r$ before it rises to the peak, and also the rates of slope from the peak, by differentiating the preceding equations.

When there is no previous knowledge of the values of the q's or of the intensities, a complete mathematical analysis of the curve is extremely difficult when there are

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several components, and this will not be attempted in the present paper in any individual case; but much information can be derived by taking definite cases of the Stark effect and plotting the results which the present wedge should give. This is a more rapid method than direct calculations for determining the essential features which the curve should present under various circumstances.

In his most recent paper, STARK has given the details of the various components of H_α as follows, although, in view of the difference in the conditions, we must not expect them to appear without serious modification in the present experiments. Under a field of 104,000 volts/cm. STARK finds for H_α:

	No. of component.	Separation (Å.U.).	Intensity.
p components	+3	+11·5	1·2
	+2	+ 8·8	1·1
	+1	+ 6·2	1·0
	−1	− 6·2	1·0
	−2	− 8·8	1·1
	−3	−11·5	1·2
s components	+1	− 2·6	1
	0	0	2·6
	−1	− 2·6	1

Now if a broadened line has an intensity I at its centre, and follows the simple exponential law, the quantity of energy in it is proportional to

$$I\int_0^\infty e^{-qx}\,dx = I/q.$$

STARK's lines are not broad, and intensity in such a case is rather a measure of contained energy than of central brightness, whatever the mode of measurement. The last column of STARK's table, therefore, may be taken as a measure of I/q where I is the central brightness of a line. The distinction is immaterial if q is the same for each component.

Now for the wedge adopted, it was known that if an intensity I_1 passing through emerged as I_2, and if

$$\log_{10}(I_1/I_2) = X,$$

then $X = 0{\cdot}2+0{\cdot}4y$, where y was the distance from the thin end, which was not indefinitely thin. But

$$I_2 = I_1 e^{-\rho y \tan\alpha} = I_1 \,.\, 10^{-\rho y \tan\alpha \,.\, \log_{10} e},$$

and therefore

$$\rho \tan\alpha = 0{\cdot}4/\log_{10} e = 0{\cdot}922,$$

or practically unity.

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The form of the curve for H_α, and in fact of all curves obtained, is not consistent with the supposition that q is the same for all components. There are two alternatives to consider in a very simple proof. If the separations are very minute, all points on the contour not between two components—or in other words all points except very close to the vertex, are outside all the component axes, and if q were constant throughout, all the boundary beyond a small distance from the vertex would take the form

$$I_c e^{\rho y \tan\alpha} = \left(I_0 + 2 \sum_{r=1}^{4} I_r \cosh q\sigma_r\right) e^{-qx},$$

and be entirely straight. This is not the case. In the second place, if the separations were comparable with STARK'S, the initial part of the curve would be

$$I_c e^{\rho y \tan\alpha} = I_0 e^{-qx} + 2 \sum_{r=1}^{4} I_r \cosh xq \,.\, e^{-q\sigma_r},$$

and $dy/dx = -q/\rho \tan\alpha$ at $x = 0$, whereas near $y = 0$ in the final part of the curve outside all the component axes, the slope is again $-q/\rho \tan\alpha$. The initial and final slopes should therefore be equal whatever the nature of the kinks. This does not occur, and we must therefore conclude that *the rates of attenuation of components are different.* The same conclusion can be deduced in other ways from the curves. The rate of attenuation of the central component is given by the initial slope in all cases, if the separations are not so extremely small as to make this an indefinite quantity. From the photographs of H_α in the present experiments we find as the mean of several measurements,

$$\rho \tan\alpha/q = 0{\cdot}057,$$

whence $q = 16{\cdot}2$ for the central component, since $\rho \tan\alpha = 0{\cdot}922$.

It has been taken for granted that the separations in H_α are not minute, in accordance with later work. The detailed description of H_α will follow, our present object being the derivation of results applicable in general to the whole series of curves, with H_α as a convenient illustration.

The values of q decrease as the separation of the components increases. This can be deduced from the fact that the final slope of all the curves to the axis of x (the base of the photograph) is smaller than the initial slope. For the final slope is derived from the final branch,

$$I_c e^{\rho y \tan\alpha} = I_0 e^{-xq_0} + 2 \sum_{r=1}^{n} 2I_n \cosh q_n\sigma_n \,.\, e^{-xq_n},$$

and

$$-\rho \tan\alpha \frac{dy}{dx} = \left\{I_0 q_0 e^{-xq_0} + 2 \sum_{1}^{n} I_n q_n \cosh q_n\sigma_n \,.\, e^{-xq_n}\right\} \Big/ \left\{I_0 e^{-xq_0} + 2 \sum_{1}^{n} I_n \cosh q_n\sigma_n e^{-xq_n}\right\},$$

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or if $I_n/q_n = E$, the measure of energy contained in a component determined by STARK'S tabular intensity,

$$-\rho \tan\alpha \frac{dy}{dx} = \left\{E_0 q_0^2 e^{-xq_0} + 2\sum_1^n E_n q_n^2 \cosh q_n \sigma_n \, . \, e^{-xq_n}\right\} \Big/ \left\{E_0 q_0 e^{-xq_0} + 2\sum_1^n E_n q_n \cosh \sigma_n q_n \, . \, e^{-xq_n}\right\},$$

whereas the initial slope is given by

$$-\rho \tan\alpha \, dy/dx = q_0.$$

The difference, which reduces to

$$\left(2\sum_1^n q_n (q_0 - q_n) E_n \cosh q_n \sigma_n e^{-q_n x}\right) \Big/ \left\{E_0 q_0 e^{-xq_0} + 2\sum_1^n E_n q_n \cosh \sigma_n q_n \, . \, e^{-xq_n}\right\},$$

must be positive, which can only be the case in general if $q_0 > q_n$. Thus *when a line showing the Stark effect is broadened, the components become more diffuse in the order of their separations in general.* Their energy is more spread out, and even if two components have the same tabular intensity in direct methods of resolution as fine lines, their heights on the photographs by the present method of the condensed discharge may be very different. For these heights are not determined by the energies in the components, but by their central intensities, which are proportional to their rates of attenuation q. It is now possible to understand at once the reason for the absence of peaks in the curve for H_α even when the energies of all the components may be strictly comparable with that of the central one. This increase of "spreading" of the components with their distance from the centre is to be expected from the fact that the change in frequency of the radiation from a specified particle depends on the degree of proximity of other charged particles, the distribution of which is subject to variations. If the arrangement of luminous and charged particles were not subject to some probability distribution, we should find sharp components as in STARK'S experiments.

(IX.) *Details of the Components of* H_α.

The theoretical boundary of the curve for H_α, on the basis of STARK'S results, has been plotted for various values of q attached to the different components, in order to discover the dependence of the curve upon these values. For values at all nearly equal, the curve consists of a series of sharp peaks of nearly equal height, separated by deep hollows; and it is evident, therefore, that the decrease in the value of q as the components separate from the central one is rapid. In these circumstances, the kink in the curve loses its peak-like character and becomes a mere protuberance. Moreover its shape for any component ceases to depend to any extent on any other component but the two adjacent, and more particularly the upper one. The

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illustrative case which has been selected is a fair approximation to the actual case of H_α, and contains both varieties of kinks. It is the upper part of the curve based on STARK's numbers for intensity and separation, magnified in the ratio 33 : 1 from the original theoretical photograph, and with a total height of 198 cm., arbitrarily selected, as the approximate height of the H_α photograph. The initial slope is taken also as that of the photograph, so that $q_0 = 16{\cdot}5$ and $\rho \tan \alpha = 1$. (q_1, q_2) for the first two other components are taken arbitrarily as 5 and 2, and (q_3, q_4) still smaller, so that they have no appreciable effect on the first two kinks.

The figure (fig. 6) exhibits the result of the calculations, the details of which are fairly obvious. The heights of the kinks are calculated and the slopes of the two

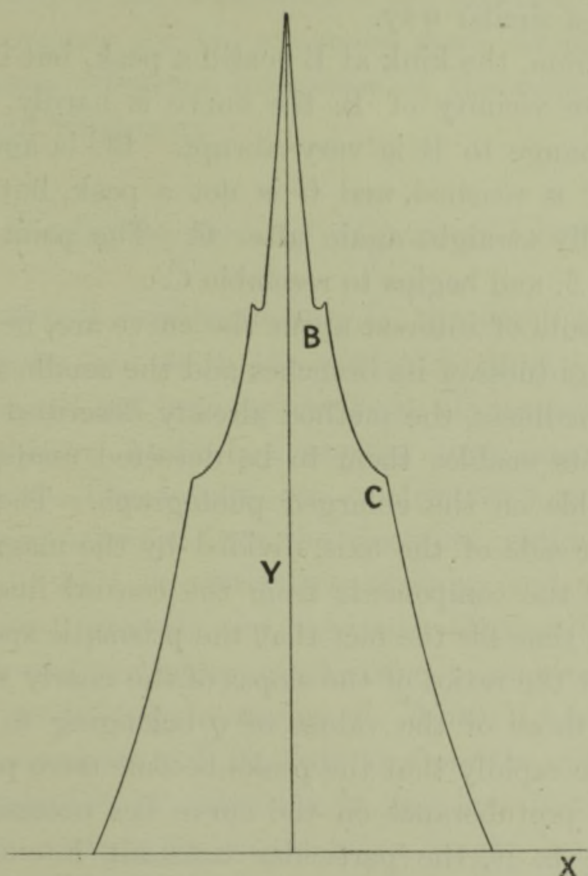

Fig. 6.

branches at each. The trough preceding the first kink is calculated as a minimum height on its branch, and other points are plotted from the equations in the ordinary way.

STARK gives the central component an intensity 2·6, and the next two an intensity 1 each. These are energy measures, and the central intensities of the broadened components are proportional to $2{\cdot}6q_0$, $5q_1$, $2q_2$, or 42·9, 5, 2 respectively, and are represented by these numbers on a certain scale. The whole height, h, of the curve of intensity I_c is given by

$$I_c e^h = 42{\cdot}9 + 2\,(5e^{-5\sigma_1} + 2e^{-2\sigma_2}),$$

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and $h = 198/33 = 6$ mm. on the original photograph, whence I_c is known on the same scale. The separations σ_1, σ_2 are those of STARK reduced to millimetres on the basis 10 Å.U. = 1 mm. valid in these experiments, and become $\sigma_1 = 0{\cdot}26$ mm., $\sigma_2 = 0{\cdot}62$ mm.

The heights of the two kinks are h_1 and h_2, where

$$I_c e^{h_1} = 42{\cdot}9e^{-16{\cdot}5\sigma_1} + 2\left\{5 \cosh 5\sigma_1 \,.\, e^{-5\sigma_1} + 2 \cosh 2\sigma_1 \,.\, e^{-2\sigma_1}\right\},$$

$$I_c e^{h_2} = 42{\cdot}9e^{-16{\cdot}5\sigma_2} + 2\left\{5 \cosh 5\sigma_1 \,.\, e^{-5\sigma_2} + 2 \cosh 2\sigma_2 \,.\, e^{-2\sigma_2}\right\}.$$

Multiplication by 33 gives the heights on the enlarged photograph. The values of dy/dx are calculated in a similar way.

In the resulting diagram, the kink at B is still a peak, but its height is very small. Down to the immediate vicinity of B, the curve is hardly distinguishable from a straight line, and its change to B is very abrupt. BC is again practically straight until the vicinity of C is reached, and C is not a peak, but a protuberance. The curve becomes practically straight again after C. The point B ceases to be a peak if q_1 is rather less than 5, and begins to resemble C.

Perhaps the main points of interest about the curve are, next to its approximation to that for H_a, the straightness of its branches and the smallness of the protuberances. But, in spite of their smallness, the method already described of using paper printed in a pattern of fine dots enables them to be detected readily by pricking out the final dot which is visible on the enlarged photograph. The distance between the protuberances on either side of the axis, divided by the magnification, gives at once twice the separation of the components from the central line on the original plate, and allows at the same time for the fact that the prismatic spectrum is not normal.

It is to be noted that the ratios of the slopes of the nearly straight branches of the curve differ little from those of the values of q belonging to the components, when these values decrease so rapidly that the peaks become mere protuberances.

Since the head of a protuberance on the curve lies necessarily on the axis of the component giving rise to it, the particular constant intensity which defines the contour is immaterial. If, therefore, a set of contours of various constant intensities are chosen on the plate, the heads of the various protuberances, one on each contour, due to any component, lie on a straight line parallel to the axis of the contours, or perpendicular to the base of the photograph. Protuberances of very small size can in this way be detected as such, without the risk of including slight irregularities in the contour which might be due to defects in the grain of the plate, and at the same time, the axes of the components can be defined with some degree of precision.

We now come to the precise values of the separations determined from the photographs of H_a. The contour exhibits three definite protuberances on each side at the same heights, and satisfying the conditions just specified. On one of the

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photographs of magnification 20·3 the breadths between the protuberances are 10·8, 23·0, and 35·5 mm., respectively. These are in the ratios 1 : 2·13 : 3·29. The separation of the three closest components in STARK's experiments* are 2·6, 6·2, and 8·8 Å.U., which are in the ratios 1 : 2·38 : 3·29. The agreement is striking. Moreover the separation of the next component in STARK's experiments is 11·5 Å.U., from which we deduce that the breadth at the next protuberance should be 47·7 mm. But the whole breadth of the base of the photograph is about 39 mm., and therefore with the degree of exposure given this component could not appear. The existence, therefore, of components whose separations are in the same ratio as those found by STARK appears to be established, and affords a strong confirmation of the view that the main factor which controls the broadening is the electrical resolution of the lines. The corresponding phenomena for H_β are much more complicated, and the determination of the attenuation-ratios and intensities of the components may, therefore, be deferred for subsequent treatment.

(X.) *The Diffuse Series of Helium and Lithium.*

The intensity distribution in broadened lines in the spectrum of helium has been investigated in the same manner as in the case of hydrogen, but the quantitative intensity distribution has not yet been determined. The spectrum was produced by passing condensed discharges through a vacuum tube containing helium with a spark-gap in the circuit. The results are qualitatively in accordance with the intensity distribution to be expected from the electrical resolution of the lines. The broadening of the line $\lambda = 4471$ is particularly striking, and it appears to consist of a bright component of great intensity and a broader displaced component. STARK* has found that the electrical resolution of this line is unsymmetrical and that the intensity of the central components is very small. Since it has been shown that the breadth of a component increases with its distance from the unresolved line, we should expect the above distribution of intensity in the line $\lambda = 4471$. On the other hand, the line $\lambda = 4026$ appears to consist of a bright central component with nebulous "wings," which is also in agreement with theory.

It may be mentioned that by the use of the wedge method the relative differences in the intensities of the lines which occur when a condensed discharge or an uncondensed discharge is employed can at once be seen. In the case of helium this is particularly interesting. With the condensed discharge the two diffuse series are relatively much more intense than with the uncondensed discharge. It is remarkable also that by far the greatest increase in relative intensity is found to occur in the line $\lambda = 4471$, whilst the D_3 line, the preceding member of the series, is affected to a smaller degree. This result, whilst affording no explanation, indicates the possibility

* *Loc. cit.*

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of reproducing in the laboratory the intensity relations which are found in the spectra of certain stars, in some of which the line $\lambda = 4471$ is the most intense of the helium lines seen, whilst under ordinary conditions of excitation by uncondensed discharges at moderate pressures the D_3 line is the strongest line in the spectrum, and at low pressures the line $\lambda = 5015$ becomes the most conspicuous.

An investigation of the lines of the diffuse series of lithium with the use of the neutral wedge has not yet been made, but qualitative results for these lines, photographed with the concave grating spectrograph, confirm the view that the Stark effect is mainly responsible for the phenomena observed. It is, of course, impossible to control the experimental conditions when spectra are produced in the electric arc, and the results may be complicated by reversal. The peculiar character of these lines has been noted by numerous investigators. More especially the complex appearance of the line $\lambda = 4602$ has been investigated by HAGENBACH* and by RAMAGE.† If the vapour is dense, reversal may be observed in the line $\lambda = 6103$. For less dense vapours the line $\lambda = 6103$ is not reversed nor the line $\lambda = 4132$, but the line $\lambda = 4602$, which belongs to the same series and lies between these lines, gives the impression of an extremely unsymmetrical reversal. These appearances of the three lines have been recorded photographically on the same plate, using as a source of light a carbon arc containing a suitable quantity of lithium. It would appear extremely improbable that the apparent reversal of the line $\lambda = 4602$ is real, since the lines preceding it and following it in the series do not show the phenomenon. This result, however, is precisely what we should predict on the supposition that the appearance of the lines depends mainly on the Stark effect.

According to STARK (*loc. cit.*) the electrical resolution of $\lambda = 6103$ consists of a small displacement, but this result is probably incomplete. For the line $\lambda = 4602$ the central undisplaced components, when the line is resolved, are either very weak or absent, and the displaced components are unsymmetrically arranged with respect to the unresolved line in the same direction as the asymmetry of the line as seen in the arc. In the case of the line $\lambda = 4132$ there are components of considerable intensity very slightly displaced from the unresolved line. A minimum unsymmetrically localised in the broadened line is therefore precisely what we should expect for the line $\lambda = 4602$, a phenomenon which we should not expect, and do not find, in the lines $\lambda = 6103$ and $\lambda = 4132$. In cases such as this, it is not improbable that the broadening of the lines may be affected by the potential fall between the poles of the arc, and indeed such phenomena as the "pole effect," or the small changes of wave-length which have been found to occur in the neighbourhood of the poles of the arc, may ultimately be explained in this way. In this case any contribution to the phenomenon of the direct action of the potential fall between the poles might be detected by polarizing the light. It may also be necessary to consider whether many

* 'Ann. d. Phys.,' (4), 9, p. 729, 1902.

† RAMAGE, 'Roy. Soc. Proc.,' vol. 71, p. 164, 1903.

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apparent cases of reversal are not in fact spurious, having no relation to true reversal, due to absorption.

Finally, the different character of lines of the same series in the spectra of the alkaline earth metals which has been noted by ROYDS* may be expected to fall into line with their electrical resolution when the necessary data are available.

(XI.) *Ultraspectroscopic Analysis by Means of the Neutral Wedge.*

It may be mentioned that the neutral wedge as an accessory to the spectroscope virtually increases its resolving power. The intensity distribution of the image of an infinitely narrow line, as seen in a spectroscope of known resolving power, is precisely defined, and analysis by means of the neutral wedge enables us to build up a system, both as regards position and intensity, which conforms with the curve experimentally found. It is therefore evident that with this accessory the practical resolving power of the spectroscope depends only on its dispersion, and is independent of the theoretical purity of the spectrum. In conjunction with the interferometer it may be expected to give results beyond the attainment of pure spectroscopic analysis.

It may reasonably be hoped that the application of such methods may enlarge our knowledge of the structure of the finest spectrum lines.

(XII.) *Summary.*

(1) A method has been described, involving the use of a neutral-tinted wedge, by means of which the actual distribution of intensity in broadened spectrum lines can be accurately measured.

(2) With this arrangement quantitative measurements of the hydrogen line H_α have been made, and qualitative observations of other lines of hydrogen, helium, and lithium.

(3) The intensity distribution of lines, broadened by condensed discharges and at high pressures, does not follow the well-known probability law, which is known to obtain under certain specified conditions.

(4) The broadening of H_α is symmetrical.

(5) The most general characteristic of all the curves obtained is that their curvature is away from the axis perpendicular to the wave-length scale. It is shown that even in the case of a simple curve, such as that found for H_α, this is inconsistent with the view that a single component is involved.

(6) The existence of more than one component is in accordance with the view that the electrical resolution of the lines is the origin of their broadening.

(7) On the supposition of several components, symmetrically distributed about the

* *Loc. cit.*

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centre, the only general law consistent with the distribution of curvature is that of a sum of linear exponential terms, one for each component.

(8) It is shown that under these circumstances discontinuities in the slope of the curves must occur. The discontinuities which have been found in the curve for H_α are in quantitative accordance with those to be expected from the available data with respect to the electrical resolution.

(9) Qualitative observation of H_β, H_γ and the diffuse series of helium and lithium confirms the view that electrical resolution is the principal cause of the phenomena.

(10) A discussion of further applications of the method is given.

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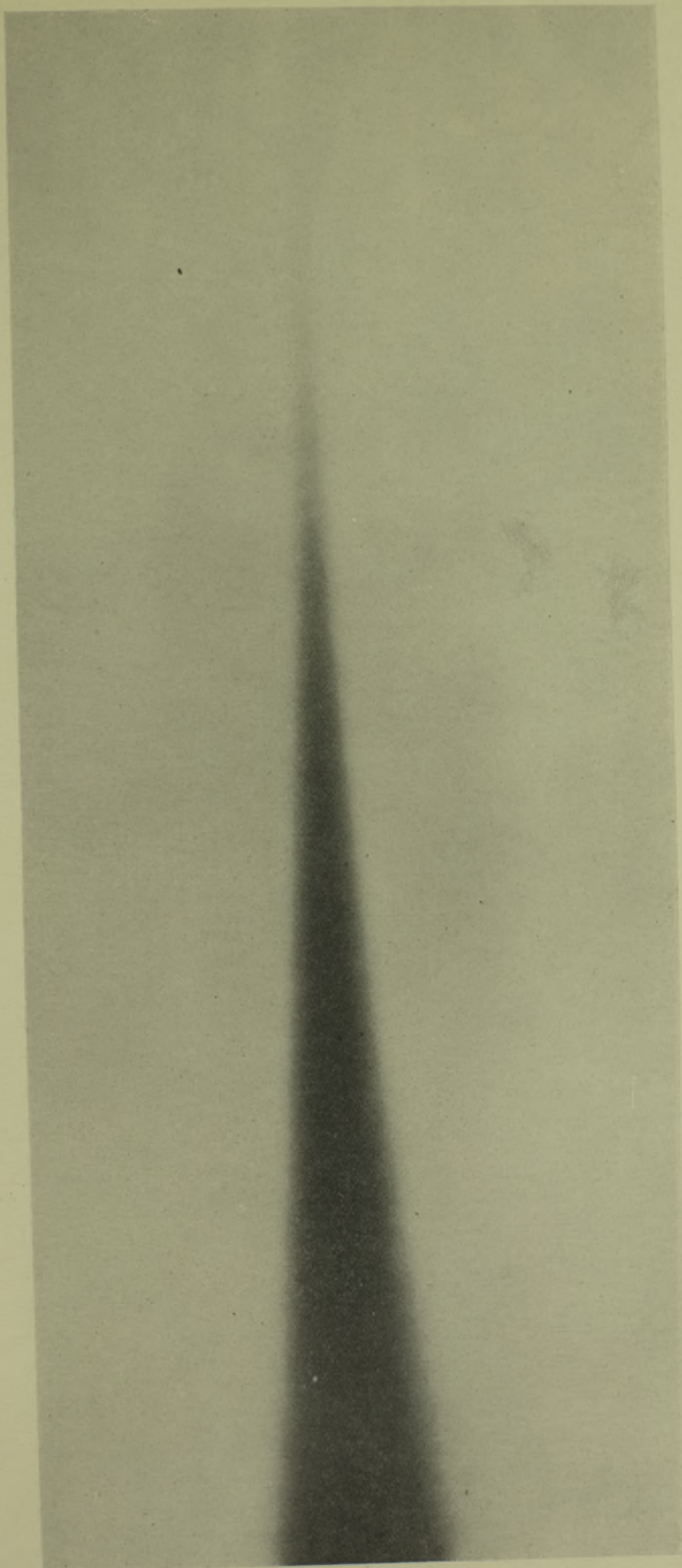

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