POTENTIAL DISTRIBUTIONS IN THE CROOKE'S DARK SPACE

POTENTIAL DISTRIBUTIONS IN THE CROOKES DARK SPACE AND RELATIVE INTENSITIES OF STARK EFFECT COMPONENTS OF H_{β} AND He λ 4922.

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SECTION A - POTENTIAL DISTRIBUTIONS

I. Introduction:

Work on the distribution of charge and of electric fields in gas discharge tubes has been carried on along various lines since about 1880, three principal methods of experiment being followed, viz: the probe method, cathode ray deflection, and the measurement of the separation of spectral lines in Stark effect photographs.

The earliest measurements were made by Hittorf[1], Graham[2], Herz[3], H. A. Wilson[4] and others, all of whom used the probe method. This consisted in placing a wire at various points along the line of discharge, observations of the potential difference between the wire and one electrode giving the distribution of potential throughout the tube. Graham improved the method by introducing two exploring electrodes at a distance _d_ apart. The difference of potential E between the two wires was measured at all points along the tube and the field determined from the values E/d thus obtained.

The principal weakness of this method lies in the inability of the probe to attain the potential of the gas without disturbing the natural field in the tube. This trouble occurs when very low pressures are used and when the conductivity is low, as in the Crookes dark space. In such a case there

there may be an abundance of negative ions and no positive ions, with the result that the wire receives negative electricity until it repels negative ions from striking it, the potential being possibly lower than it would be at any point in the tube if the probe were not introduced.

J. J. Thomson suggested using the deflection of a cathode ray beam as a measure of field strengths in vacuum tubes. In this case the cathode beam was supplied by a secondary tube perpendicular to the direction of the discharge, which projected it through a small cylindrical anode, through the field of force to a willemite screen. Assuming the field to be uniform over any cross section, and to exist over a thickness $\underline{d}$, the deflection $\underline{\delta}$ of the trace of the beam on the screen, distant $\underline{\ell}$ from the edge of the discharge, is given by:

$$\delta = \frac{X}{2V} d \left(\frac{d}{2}+\ell\right)$$

where **V** is the voltage producing the beam and **X** is the field strength measured in volts per cm. The beam, having been localized in passing through the anode, gives a clearly defined spot on the screen, so that the method leads to fairly accurate determinations throughout the main part of the discharge, as seen by the agreement in the results of Aston[6], Harris[7] and Schuster[5] and others.

The third method is especially good for measuring high fields such as are always found near the cathode in the Crookes dark space. Based on spectroscopic work, it is extremely accurate and very free from experimental error. The displacement of Stark effect components of any of the Balmer lines of hydrogen are measured, and may be compared either with the experimental results of Stark[9] or with the theoretical work of Epstein[10] and Schwartschild[11]. Stark, using a type of canal-ray tube with the auxiliary electrode at a known distance from the perforated cathode, measured the displacements of the components of some of the Balmer lines under known electric fields; and established a relation between the separation and the field strength which is at once applicable to field measurement in any style of discharge tube, where the field is high enough to produce a measurable Stark effect. The theoretical work referred to is in good agreement with the experimental results and may be used as an alternative source of information in calculating field distributions from Stark effect photographs. The formula, due to Epstein, obtained from quantum dynamics for an $(n_1 n_2 n_3) \rightarrow (m_1 m_2 m_3)$ transition is given by:

$$\Delta \nu = \frac{3hE}{8\pi^2 me z}\,(n_1 - n_2)\,(n_1 + n_2 + n_3) - (m_1 - m_2)\,(m_1 + m_2 + m_3)$$

where E is the field strength, z is the nuclear charge, m and e refer to the mass and charge of an electron, and h is Planck's constant. This method has been applied to fields in the Crookes dark space by LoSurdo[12], Nyquist[13], Brose[14], Foster[15], Anderson[16], Takamine[17], and Yoshida[18] and some very interesting results have been published.

The general nature of the field distribution is well known. Near the anode there is a fairly sudden change in potential known as the anode fall. Throughout the positive column the force is practically constant, slight alternating variations occurring when striations are present, the maxima corresponding to the bright parts of the striae and vice versa. Through the Faraday dark space the force gradually diminishes, reaching its minimum value at the edge of this dark space or in the negative glow. There is then a very sudden increase, and the electric force becomes very large in the Crookes dark space as the cathode is approached. The sudden increase in the field near the cathode was noted by all investigators, a great excess of positive ions existing in this part of the tube, with a surface layer of electrons very close to the cathode.

The nature of the cathode was found to affect this cathode fall very considerably. Hittorf[19] showed that the fall became exceedingly small when the cathode was raised to red heat. Goldstein[20], however, found later that after the heating is continued for some time it grows again. Mey[21] found the fall to be lower for the more strongly electro-positive alkali metals; but after the discharge has gone on for some time it increases to a value which is found to be independent of the metal used. This is attributed mainly to the fact that after being used for some time all oxides are freed from the surface. Certain metals are much less appropriate than others, however, because of excessive sputtering, and Aluminium, which sputters very little, has consequently been used a great deal in all these investigations.

Wehnelt[22] stated that the electric force in the dark space was influenced by the walls of the tube when the diameter of the tube is small. His work indicates that in cylindrical tubes the equipotential surfaces are approximately planes near the cathode, perpendicular to the axis of the discharge. As the distance from the cathode is increased they become cap-shaped extending nearer to the anode at the centre than at the edges, this distortion being due to the electrification on the walls. Harris[1] also states that at low pressures the equipotential surfaces are certainly not planes, and Takamine and Yoshida attribute the diffuse character of their Stark-effect photographs partly to this fact. Photographs taken by Foster[15], on the other hand, show extremely sharp Stark-effect components, indicating that the field must be exceedingly uniform over all cross sections in the dark space.

A number of formulae have been put forward to express the field distributions in the dark space, but up to the present no general mathematical theory has been worked out which will express the distribution in terms of the shape of the tube near the cathode.

It is generally found that large fields can most easily be obtained with tubes of small diameter.

Aston,[6] by means of cathode ray deflection, measured the distribution of electric field in front of very large plane cathodes, in tubes whose walls were far enough from the electrodes to be without effect on the discharge. He found that the electric force was proportional to the distance from the edge of the negative glow.

Similar results were obtained by Anderson[16] and Lo Surdo[12] using the Stark effect method in very different styles of tubes. Anderson used the metal whose Stark effect he was studying as a cathode, and had it fitted loosely into a short silica tube in the centre of a bell jar 15 cms. in diameter, the anode being inserted into the top of the jar. Lo Surdo used a discharge tube having the section into which the cathode was inserted of relatively small diameter. Here one would expect the walls to produce an effect if ever they do, but the photographs show none.

Schuster and Graham found that the electric force increased very rapidly close to the cathode, but was very appreciable throughout the dark space. Schuster[9] obtained a formula connecting the fall of potential between the cathode and a point in the Crookes dark space or negative glow with the total cathode fall in the form:

$$V = V_0 \left(1 - \epsilon^{-\kappa x}\right),$$

where V_0 is the cathode fall and κ a constant depending on the pressure. Since $\frac{\partial^2 V}{\partial x^2} = 4\pi\rho$ where ρ is the density of free electricity, this distribution would involve the existence of positive charge of electricity whose density decreases in geometrical progression as the distance from the cathode increases in arithmetical progression.

Takamine[17] and Yoshida[18], working on the Stark effect, used a modified Lo Surdo tube consisting of a spherical glass bulb into which two tubes were sealed on opposite sides. Into these were fitted the anode and cathode respectively. The radii of the tubes containing the cathode varied from one and a half to sixteen millimeters, and in all cases a parabolic distribution was obtained given by:

$$E - E_0 = k\,(d - d_0)^2$$

where d_0 is the length of the dark space, and E_0 is the electric force at the end of the dark space, d is the distance from the cathode of the point at which E is measured, and k is a constant for any tube, decreasing as the diameter of the tube increases. No information is given, however, as to the nature of the discharge in these tubes or as to how the cathode is pitted.

Some very careful work on the field strengths just in front of the cathode was carried out by Brose,[14] who examined the separation of the Stark effect components of H and applied Stark's results. Cylindrical tubes of different diameters were employed, the electrodes being of aluminium. He tabulates and graphs his results for different diameters and lengths of the dark space. They show that in the immediate neighbourhood of the cathode the field has a large value which increases to a maximum at a little distance from the cathode and then falls away gradually to a very small value towards the negative glow. This distribution is in strict accordance with the results obtained by Nyquist[13] and Foster,[15] both of whom used modified Lo Surdo tubes. In Nyquist's tube the section near the cathode was made of aluminium, insulated from the cathode by a thin glass tube, while Foster improved on this type by making the cathode fit snugly into a section of lavite which could be sealed directly into the main tube. The discharge giving rise to this distribution takes place to the centre of the cathode in which a very definite pit is formed.

Yoshida has pointed out the possibility that the distribution may depend on the source of high potential used, varying in accordance with the degree of rectification of the current, and smoothness but this has not yet been tested.

The purpose of the investigations of the writer has been to study further the effect of the shape of the tube near the cathode on field distributions in the Crookes dark space. The fields being high, the Stark effect method was used as being most free from sources of error. Tubes of a modified Lo Surdo type were employed and the effect of a sudden change in the diameter of the tube was studied. A test was also made on the variation in the field over the whole cross section of the discharge in this part of the tube.

II. Description of Apparatus:

Discharge tubes of a modified Lo Surdo type were employed in the investigation, the aluminium cathode being fitted into a plug of lavite which was sealed into the main tube. The advantage of this type of tube lies in the fact that the lavite can be turned in a lathe and a tube can thus be obtained in which the shape and dimensions are known accurately. The side window was put on at some distance from the discharge thus eliminating any effect of sputtering of the cathode. The tube, which was in all cases made of pyrex, was connected by a wax joint to a glass vacuum system (Fig. 1) consisting of a charcoal bulb, McLeod gauge and large ballast bulb for the purpose of keeping the pressure constant during an exposure. The arrangement of the vacuum outfit is seen from the diagram. The gauge G has a 100: 1 ratio giving the pressure quite accurately enough for the work being done. The charcoal bulb K is of pyrex made so that the gas may be forced to go through the charcoal on its way from the container H to the tube. The charcoal is held in the outer section by means of glass wool. The seals to the remainder of the apparatus are of wax. The gas required is admitted at atmospheric pressure through the stop-cock A, A hy-vac pump is attached at B, and the stop-cock C is put in so that the gas may be kept pure when the tube is not set up. The gas was purified by immersing the charcoal bulb in liquid air.

The light from the discharge is emitted from a narrow slit cut in the lavite. It is then passed through a double image prism and the images of the two polarizations (parallel and perpendicular to the field) thus obtained are focussed by means of a Zeiss lens on the collimator slit of the spectrograph. A $\lambda/4$ quartz plate was placed in the path of the beam polarized parallel to the direction of the slit in order to rotate the plane of polarization through a right angle and thus minimize reflection from the prism faces.

A six prism glass spectrograph with a dispersion of 6.6 Å per mm. at H_β, and a theoretical resolving power of .3λ, was used. The prisms are placed in a closed box on a heavy plane steel table. In the centre of this there is a small glass thermostat connected to three heating elements supported underneath the prism table, and to an electrical relay outside. The current flow in the heating elements is thus regulated by the temperature inside the box, and, the temperature being kept constant, all strains in the glass prisms are eliminated. This correction is necessary on account of the size of the prisms used, the faces being 5.6 × 10.3 cms. The collimator and camera lenses are doublets of 45 inch focal length and aperture large enough to take in all the light which comes through the prisms.

The electrical apparatus supplying the high potential across the tube is shown in Fig. II. It consists essentially of a step-up transformer, raising the voltage from 110V to values as high as 10,000V, together with two kenotron rectifiers K, and capacities C, equal to 1.4 μf each, and 400 henry inductance L, the capacities and inductance being used to make the current free from ripples. The resistance R_1 regulates the current in the kenotron filaments, as determined from a voltmeter across the kenotron primary not shown in the diagram; and R_2 regulates the potential across the discharge tube T. R_3 is a water resistance in series with the tube to keep the discharge steady, A a milli-ammeter giving the current through the tube, and V an electrostatic voltmeter giving the voltage between the terminals. This apparatus gave a very steady source of high potential and proved satisfactory in every way during all the experimental work undertaken.

III. <u>Experimental Procedure and Results</u>:

The first tube was of the type shown in Fig. III. The small cylindrical cathode, 2.4 mm. in diameter, fitted into the lavite section of the tube, both the aluminium and lavite being threaded so that the position of the cathode could be determined accurately. A brass screw driver embedded in wax in the ground glass joint served to move the cathode, the number of turns being read by a scale on the outside of the tube. The slit in the lavite was cut narrow to prevent it affecting the field.

This tube was used with pure hydrogen, the gas being admitted to the large bulb in the vacuum outfit and purified with charcoal and liquid air. The spectrograph was focussed with the H_α line at the centre of the plate, and the shape of the Stark effect p-and s-components was either photographed or noted visually for various distances of the cathode from the shoulder. The distance was calculated from the number of turns of the ground glass joint, read on the scale on the outside of the ground glass joint, the pitch of the thread in the aluminium and lavite being known. The p-components, giving a larger separation, were used in estimating the distribution of potential.

In this work it was found that, when the cathode was flush with the shoulder of the small section of the tube, the field strength varied directly with the distance from the cathode, becoming practically zero at the end of the dark space. This distribution is what one would expect where the walls are far away from the cathode stream of electrons, and is in agreement with the work of Aston for large tubes and large cathodes where the wall effect is inappreciable. There was, however, a slight decrease in the field very close to the cathode due possibly to an excess of negative ions just at the cathode surface.

Photographs taken with the cathode at different distances from the shoulder, showed that in a tube of the above type in which the length of the dark space exceeds or is approximately equal to the length of the small section, the field inside the tube is practically uniform. This was found true, except for the slight fall at the cathode surface, for positions of the cathode varying from 1/2 to 2 mm. from the shoulder. The length of the dark space was estimated from the appearance of the discharge, looking directly through the slit in the lavite section of the tube. It was most interesting to note that the sudden change in the diameter of the tube in the vicinity of the dark space produced no sudden change in the field strength, the maximum field merely being reached more quickly and existing over a longer distance as the dark space was drawn into the tube by lowering the cathode. Variation of pressure from 1/2 to 1-1/2 mm. in case of cathode being flush with the shoulder was found to produce no change in the character of the distribution, though the dark space grew longer when lower pressures were tried owing to the increase in the free path. It should be noted that in all this work the edges of the cathode were made just free of the walls, and all the discharge took place towards the centre of the cathode face.

According to current ideas concerning the origin of the dark space, practically no recombination occurs in this part of the discharge.

Thus, by restricting the discharge to a very small tube we should expect practically all the gas to be ionized and taking part in the actual discharge. If that is the case we should expect the fall of potential to correspond to the fall along a metal conductor, a constant field existing at all points. This idea seems to be confirmed by the experiment except for the slight surface effect at the cathode.

The second type of tube,(Fig. IV.) used in this part of the work was designed to show whether the field is constant over the whole of the surface of the cathode, i.e. whether the equipotentials are planes perpendicular to the axis of the tube or not. To do this the cathode was made rectangular in cross section, (area 2.2 x 7.2 mm.) fitting into a lavite plug as before. The slit was cut acorss the tube parallel to the cathode surface and opposite to the longer side of the cathode, and the separation of the Stark effect components corresponding to light from different parts of the dark space just in front of the cathode was measured. The tube was of necessity used in a horizontal position in this case, instead of vertical as in the previous work. The cathode was threaded and held in place by two lock nuts; the aluminium piece was screwed on to a brass head which in turn was soldered to a flexible piece of piano wire. A small brass rod at the other end fitted against a light spring in a brass tube which was fastened to a piece of lavite in the inner section of the ground glass joint. Connection to the electrical outfit was made by tungsten wire sealed through the pyrex.

Hydrogen was again used in the tube and after re-focussing, photographs were taken of the H_β components. The light was very carefully focussed on the slit of the collimator so as to ensure having the light from each part of the tube correspond to a definite section of the line on the plate. The photographs showed that the separation is constant over the whole length of the lines,and, therefore, the field may be assumed constant over the whole cathode surface.

At this point in the work it was thought advisable to drop the investigation of potential distributions in other types of tubes and to make a direct application of the results obtained.

SECTION B.

RELATIVE INTENSITIES OF STARK EFFECT COMPONENTS

I. Introduction:

In recent years the quantum theory of line spectra, as developed by Sommerfeld, Epstein, Schwarzschild, and others in extending Bohr's original theory, has not only given rise to an explanation of the frequencies of the components, of the characteristic fine structure of the hydrogen lines and of the Stark and Zeeman effects, but has also led to some conclusions regarding the polarization and intensities with which these lines appear from a consideration of the amplitudes of the harmonic vibrations into which the motion of the electrons in an atomic system may be resolved.

Kramers[23] has worked out in detail the problem of intensity of spectral lines in thecase of the fine structure, and that of the Stark effect of the hydrogen lines and ionized helium, and compared his results with observations. The experimental work on relative intensities carried out by the writer in H_β and He λ 4922 Stark effect components has been done because of the theoretical interest in these lines; for while hydrogen has up to the present been the only element for which the theory has been fully worked out, helium being the second element in the periodic table, is clearly the next to be investigated from a theoretical point of view.

II. Theory:

Consider a mechanical system of s degrees of freedom for which the generalized co-ordinates specifying the positions of particles in space are $(q_1 \ldots q_s)$ and the canonical conjugated momenta are $(p_1 \ldots p_s)$. Then the equations of motion are given by the canonical equations:

$$\frac{dp_k}{dt} = -\frac{\partial E}{\partial q_k}, \qquad \frac{dq_k}{dt} = \frac{\partial E}{\partial p_k} \qquad (k = 1, 2 \cdots s) \tag{1}$$

where E is the total energy of the system and is assumed to be a function of the p's and the q's only. The Hamilton-Jacobi partial differential equation is then obtained by writing $p_i = \frac{\partial S}{\partial q_i}$ where S is a function of the q's and putting E equal to a constant α_1:

$$E\left(q_1\, q_2 \cdots q_s, \frac{\partial S}{\partial q_1} \cdots \frac{\partial S}{\partial q_s}\right) = \alpha_1 \tag{2}$$

A complete solution of this equation will contain an additional constant C and s - 1 other integration constants, $(\alpha_2 \cdots \alpha_s)$

For a suitable choice of orthogonal generalized co-ordinates $q_1 \ldots q_s$, it may be possible to "separate the variables", i.e. a complete solution may be written in the form

$$S = \sum S_k (q_k, \alpha_1 \cdots \alpha_s) + C \tag{3}$$

If this is the case it can be shown that S may be written in the form

$$S = \sum_1^s \int \sqrt{F_k (q_k; \alpha_1 \cdots \alpha_s)}\, dq_k \tag{4}$$

If the α's satisfy the condition that every function $F_k(q_k)$ possesses at least two successive finite real simple roots q_k' and q_k'' between which the value of the function is positive, the function S will, considered as a function of the q's, have s moduli of periodicity defined by

$$I_k = \oint \sqrt{F_k(q_k; \alpha_1 \cdots \alpha_s)}\, dq_k \qquad (k = 1, \cdots s) \tag{5}$$

Clearly the I's are continuous functions of the α's, whence

$$S = \sum_1^s \int^{q_k} \sqrt{F_k(q_k; I_1 \cdots I_s)}\, dq_k \tag{6}$$

Transforming the variables by the relations

$$p_k = \frac{\partial S}{\partial q_k}, \qquad w_k = \frac{\partial S}{\partial I_k} \tag{7}$$

it can be seen that the q's and the p's considered as functions of the w's and the I's are one-valued functions of these variables which are periodic in each of the w's with period 1. The q's may therefore be expanded in an s-double Fourier series of the form

$$q_k = \sum C^k_{\tau_1 \cdots \tau_s} e^{2\pi i(\tau_1 w_1 + \cdots + \tau_s w_s)} \tag{8}$$

summed over all values of the τ's and where the C's depend on the I's only. Similar expansions will hold for the p's.

The above transformation being a contact transformation, the canonical equations of motion are given by

$$\frac{dI_k}{dt} = -\frac{\partial E}{\partial w_k}, \qquad \frac{dw_k}{dt} = \frac{\partial E}{\partial I_k} \tag{9}$$

whence, since $E = \alpha_1$, and is consequently a function of the I's, the solution is given by

$$I_k = \text{constant} \qquad w_k = \varpi_k t + \delta_k, \quad \varpi_k = \frac{\partial E}{\partial I_k} \tag{10}$$

This system is conditionally periodic in which the w's are the angle variables and the I's are the action variables or moduli of periodicity of the system.

Considered as a function of the I's and the w's the displacement x will, like the q's, be periodic in each of the w's with period 1, and may also be expressed in a trigonometric series of the form

$$x = \sum C_{\tau_1 \cdots \tau_s} e^{2\pi i (\tau_1 w_1 + \cdots \tau_s w_s)}$$

which becomes on substition from (10)

$$x = \sum C_{\tau_1 \cdots \tau_s} e^{2\pi i \{(\tau_1 \varpi_1 + \cdots \tau_s \varpi_s) t + c_{\tau_1 \cdots \tau_s}\}} \qquad (11)$$

showing that the motion of a conditionally periodic system may be resolved into a number of harmonic vibrations of frequencies $|\tau_1 \varpi_1 + \cdots \cdots + \tau_s \varpi_s|$ the amplitudes of which depend on the quantities I_k only. In "degenerate" systems which often arise in quantum theory n of the ϖ's may be eliminated due to n relations existing of the form $\sum_1^s m_k \varpi_k = 0$ for all values of the I's where the m's are a set of integers possessing no common divisor.

The value of the coefficient C_τ arising in the above expansions can be expressed in the form

$$C_{\tau_1 \cdots \tau_s} = \sum_r \Phi_{1r} \Phi_{2r} \qquad \Phi_{sr} \qquad (12)$$

where Φ_{ir} is a definite integral of the form

$$\Phi_i = \int \varphi(q_i) e^{-2\pi i \sum_k \tau_k \frac{\partial S_i}{\partial I_k}} dq_i \qquad (13)$$

This is true only if the function

$$f(q_1 \cdots q_s) = \sum C_{\tau_1 \cdots \tau_s} e^{2\pi i (\tau_1 w_1 + \cdots + \tau_s w_s)}$$

can be expressed in the form

$$f(q_1 \cdots q_s) = \sum_r f_{1r}(q_1) f_{2r}(q_2) \cdots f_{sr}(q_s) \qquad (14)$$

i.e. if we can separate the variables. In the applications of the quantum theory the separation of the variables is always obtained in one or other set of the elliptical co-ordinates given by Jacobi.[29]

This theory is applied to the case of the hydrogen atom under the influence of a strong homogeneous electric field of force F in which the force F is assumed small in comparison with the force which the nucleus exerts on the electron. The equations of motion are derived from Newtonian mechanics, neglecting any relativity correction, and are solved by means of trigonometric series of the type (11) in such a way that in calculating the coefficients C, small quantities which are proportional to the first power and to higher powers of F are neglected. Separation of the variables is obtained by transforming to parabolic co-ordinates, defined in terms of Cartisian rectangular co-ordinates by the relations:

$$z = \frac{\xi - \eta}{2} \quad ; \quad x + iy = \sqrt{\xi\eta}\, e^{i\varphi} \tag{15}$$

where ξ and η are two parameters defining the two paraboloids of revolution which have their common focus at the nucleus and their common axis parallel to the z-axis and which pass through the electron, while φ is the angular distance between the x z -plane and the plane containing the z-axis and the electron:

Now the kinetic energy $T = \frac{m}{2}\left(\dot{x}^2 + \dot{y}^2 + \dot{z}^2\right)$

and the potential energy $P = \left(-\frac{Ne^2}{r} - eFz\right)$ (16)

where Ne is the nuclear charge of the atom.

Making the transformations (15) and (16) so that the total energy E is a function of $(\xi, \eta, \varphi, p_\xi, p_\eta, p_\varphi)$ the Hamilton-Jacobi partial differential equation is obtained by introducing $p_\xi = \frac{\partial S}{\partial \xi}$ etc., and by putting the expression for energy thus obtained equal to a constant α_1

Effect a separation of the variables by taking

$$S = S_\varphi + S_\xi + S_\eta$$

i.e. $S = \alpha_2 \varphi + S_\xi + S_\eta$ since $p_\varphi = \alpha_2 =$ Constant, being a cyclic co-ordinate.

Then three equations are obtained each depending only on one variable which integrated become:

$$\left.\begin{aligned} I_1 &= \int \frac{d\xi}{2\xi}\sqrt{-\alpha_3^2 + 2(mNe^2 - \alpha_2)\xi + 2m\alpha_1\xi^2 - meF\xi^3} \\ I_2 &= \int \frac{d\eta}{2\eta}\sqrt{-\alpha_3^2 + 2(mNe^2 + \alpha_2)\eta + 2m\alpha_1\eta^2 + meF\eta^3} \\ I_3 &= \int_0^{2\pi} \alpha_3 \, d\varphi \end{aligned}\right\} \quad (17)$$

Expanding the radicals and retaining terms of the first order only in F, integrals of known forms are obtained. Equating the I's in turn to n_1h, n_2h and n_3h, and evaluating the integrals obtained on expansion, equations result which can be solved for the values of α_1 and α_2, assuming the field zero initially.

Using these values in the terms involving the field F we at once get the energy equation given by:

$$E = \alpha_1 = \frac{2\pi^2 m N^2 e^4}{h^2(n_1+n_2+n_3)^2} + \frac{3}{8}(n_1 - n_2)(n_1+n_2+n_3)\frac{hF}{\pi^2 meN} \quad (18)$$

But by Bohr's frequency relation, $(E'' - E') = h\nu$ (19)

whence the difference between frequencies of Stark effect components and that of the original line in Hydrogen is given by:

$$\Delta\nu = -\frac{3}{8}\frac{hF}{\pi^2 meN} z$$

where $z = (m_1 - m_2)(m_1 + m_2 + m_3) - (n_1 - n_2)(n_1 + n_2 + n_3)$

Otherwise, we may get the equations for the α's in terms of the I's by expanding the integrals in powers of F and obtain the equation for S in the form:

$$2\pi S = \frac{1}{2}\int^{\xi}\frac{d\xi}{\xi}\sqrt{-I_3^2 + 2\frac{2I_1 + I_3}{\chi I}\xi - \frac{\xi^2}{\chi^2 I^2}} + \frac{1}{2}\int^{\eta}\frac{d\eta}{\eta}\sqrt{-I_3^2 + 2\frac{2I_2 + I_3}{\chi I}\eta - \frac{\eta^2}{\chi^2 I^2}} + I_3\varphi \qquad (20)$$

where

$$\chi = \frac{1}{4\pi^2 Ne^2 m} \quad \text{and} \quad I = I_1 + I_2 + I_3$$

From this equation the angle variables ω_1, ω_2 and ω_3 can be found, and by making suitable substitutions for ξ and η it can be shown that ξ and η are functions of ω_1 and ω_2 only. From this it follows that $z = \frac{\xi - \eta}{2}$ may be expanded in a doubly infinite series of the form:

$$z = \frac{\xi - \eta}{2} = \sum A_{\tau_1 \tau_2} e^{2\pi i(\tau_1\omega_1 + \tau_2\omega_2)} \qquad (21)$$

and from Fourier's theorem $A_{\tau_1\tau_2}$ can be found in terms of Bessel funtions involving χ and the I's.

By a similar process of calculation it can be shown that x + iy allows of an expansion of the form:

$$(x + iy)e^{2\pi i(\omega_2 - \omega_3)} = \sum B_{\tau_1\tau_2} e^{2\pi i(\tau_1\omega_1 + \overline{\tau_2 + 1}\,\omega_2)} \qquad (22)$$

and the coefficients B are also found, by an application of Fourier's theorem, to be given by an expression involving χ and the I's in Bessel functions which can be evaluated.

The formulae for z and $x+iy$ obtained by this process show that the motion of the electron may be regarded as a superposition of an infinite number of linear harmonic vibrations parallel to the direction of the electric force with frequencies $|\tau_1\omega_1 + \tau_2\omega_2|$, and of an infinite number of circular harmonic rotations perpendicular to this direction with frequencies $|\tau_1\omega_1 + \tau_2\omega_2 + \omega_3|$

It must be remembered that in the expressions obtained for the amplitudes of these frequencies, small quantities proportional to F and to higher powers of F are neglected. By retaining the terms involving F^2 in the expansions for the α's, found from solving between the equations (17) for the I's it is possible to deduce the second order Stark effect depending on the square of the field.

In weak fields the relativity modifications in the laws of mechanics become comparable with those due to the electric field; and if weak enough, the influence of the field on the motion of the electron may become negligible in comparison with the relativity effect. Kramers, carrying out the calculations for this last case in a manner analagous to the method described for strong fields, finds that new frequencies arise in both polarizations.

Bohr's frequency relation:

$$E' - E'' = h\nu \tag{23}$$

and the application of his theory to the simplified hydrogen atom lead to the values for the energy in the n^{th} stationary state, the frequency ω of revolution, and the major axis of the Keplerian ellipse described by the electrons under no external forces. The theories of Sommerfeld[23] for relativity correction, of Epstein[19] and Schwarzschild[20] for the effect of a homogeneous electric field, and of Sommerfeld[24] and De Bye[25] for the effect of a homogeneous magnetic field on the hydrogen lines, all indicate the fact that the stationary states of the hydrogen atom are split up into a number of stationary states in which the energy differs only slightly from the energy calculated for the simplified atom.

Thus in the case of an electric field acting on the atom the stationary states are determined by three whole numbers n_1 n_2 n_3, their sum n "corresponding" to a stationary state of the simplified atom characterised by this value n.

This theory fully determines the frequencies of the lines emitted, but the intensity and polarization clearly involve some knowledge of the nature of the vibration. Clearly, due to the discontinuous character of the transition of an electron from one stationary state to another, the process of radiation will differ from that arising in ordinary electro dynamics. Einstein[26] therefore introduces the quantum theory idea of the "a-priori probability of spontaneous transition" '$A^{n'}_{n''}$' between two states characterised by n'''s and n''s. If then ν is the frequency of the radiation emitted during a certain transition and α' the number of atoms present in the initial state, the energy of radiation of frequency ν emitted in unit time will be given by $\alpha' A'_{''} h\nu$

Bohr[21] has shown that a formal connection exists between the two theories. Between any two stationary states characterised by the quantum numbers $n'_1 \quad n'_s$ and $n''_1 \ldots n''_s$ a multitude of mechanically possible states lying between the initial and final state exist where

$$I_k = \{ n''_k + \lambda (n'_k - n''_k) \} h$$ in which λ assumes and values between 0 and 1. (24)

From (10) it follows that the difference in total energy for two neighbouring mechanically possible states is given by

$$\delta E = \varpi_1 \delta I_1 + \cdots\cdots + \varpi_s \delta I_s$$

so that from (23) we get

$$\nu = \frac{1}{h} \int_{\lambda=0}^{\lambda=1} \delta E = \frac{1}{h} \int_{\lambda=0}^{\lambda=1} (\varpi_1 \delta I_1 + \cdots\cdots + \varpi_s \delta I_s) = \int_0^1 d\lambda \left[(n'_1 - n''_1)\varpi_1 + \cdots + (n'_s - n''_s)\varpi_s \right] \quad (25)$$

Thus the frequency of the emitted radiation approaches asymptotically to the frequency present in the motion of the system for large quantum numbers

According to Bohr, we may extend this to the case of intensities and polarizations of the spectral lines emitted. In the region of large n's they will become asymptotically the same as the intensities and polarizations of the corresponding lines which one would expect from ordinary electrodynamical theory. This hypothesis is upheld by by the agreement of Planck's intensity distribution formula with that of Rayleigh and Jeans in the limit of large wave-lengths. Now according to the laws of electrodynamics, the radiation energy emitted by an electron performing oscillations of the form $x = C \cos 2\pi\varpi t$, where C is the amplitude and ϖ the frequency of vibration, would be proportional to the mean square of the aceeleration of the electron, and would therefore be given by $g\, C^2 \varpi^4$, where g is a universal constant.

Thus we may conclude that the a-priori probability of spontaneous transition between two states characterised by high quantum numbers, whose differences ($\tau_1 \cdots\cdots \tau_s$) are negligible in comparison with the numbers themselves, will be symptotically given by $g\, C^2 \varpi^4 / h\varpi = \frac{g}{h} C^2 \varpi^3$ where $\varpi = \varpi_1 \tau_1 + \varpi_2 \tau_2 + \varpi_s \tau_s$ represents the frequency of the emitted radiation and C the amplitude of the harmonic vibration of this frequency occurring in the motion of the electron in the initial or in the final state.

In regions where the n's are small numbers, we may assume, according to Bohr, that there will still exist a close connection between the coefficients C appearing in the trigonometric series of the type (11.) by which the motion of the system may be represented, and the a-priori probabilities for transitions between these states. Thus, if for the displacements of the electrons in all directions in space, the coefficient $C_{\tau_1^\circ \cdots\cdots \tau_s^\circ}$ corresponding to the frequency $\tau_1^\circ \varpi_1 + \cdots\cdots + \tau_s^\circ \varpi_s$ is equal to zero, independent of the values of the I's, the transition given by $n_1' - n_1'' = \tau_1^0 \dots n_s' - n_s'' = \tau_s^0$ will be impossible. If, however, the coefficient in question is zero only for a displacement of the electrons in one direction this transition will give rise to a radiation polarized perpendicular to this direction.

Thus we find that definite conclusions may be drawn regarding polarisations, but a close estimate of the intensity for transitions in which the n's involved are small is at present impossible. The intensities clearly depend on the a-priori probability $A_{''}^{'}$ of the transition in question, which in turn depends on the mechanical properties of the system in both the initial and final states. It is not to be expected that a simple relation between the probability and the amplitudes of the harmonic frequency $(n_1' - n_1'')\omega_1 + (n_2' - n_2'')\omega_2 + \dots\dots (n_s' - n_s'')\omega_s$ exists for small n's, but from the frequency correspondence principle (25), it may be assumed that $A_{''}^{'} = \frac{9}{h} \bar{C}^2 \nu^3$ for such a transition when $\bar{C}$ is a suitably chosen mean value of the amplitude of the vibration frequency given above. The relative intensities with which the different components of the Stark effect will appear may be estimated by comparing the intensity of each component with the values of the squares of the amplitudes of the corresponding harmonic vibrations occurring in the system in the initial and final states, and in the mechanically possible states lying between these states.

For low quantum numbers difficulty arises in deciding how the mean value $\bar{C}$ should be chosen. In Kramer's estimate the mean obtained from the value of $A_{''}^{'}$ given by

$$A_{''}^{'} = \frac{9}{h} \nu^{3-m} \int_0^1 \nu^m C_{\tau_1 \dots \tau_s} \, d\lambda$$

was used, where m is an arbitrary number and λ is the parameter arising in (24). Other means, however, which give the same asymtotic value may be found, e.g. the logarithmic mean of the amplitude given by

$$\bar{C} = e^{\int_0^1 \log C_\lambda \, d\lambda}$$

which corresponds well with the X-ray doublet data. Besides this the amplitudes must be normalized by division by the semi-major axis of the Keperian ellipse involved in the different states, since otherwise the two states would have unequal weights, the first orbit having much smaller dimensions and lower amplitudes than the initial one.

Hoyt[30] has calculated relative intensities of principal absorption lines in the hydrogen Balmer series using various formulae for $A_{n}^{'}$ but there are inadequate experimental results to test the results accurately.

Kramers emphasizes the fact that only a rough estimate of the relative intensities can be obtained, and points out, for example, that in the Stark effect certain transitions occur for which the amplitudes of the corresponding frequency are zero, whereas the intensity of the corresponding component differs from zero. In such cases it can be shown that the corresponding frequency, in the mechanically possible states lying between the initial and final states, differs from zero. In the (112) $\rightarrow$ (002) transition for

H_β, we meet with an exception to this rule, a faint line appearing in the photographs. It may not be in disagreement with the theory, however, as it is possibly due to the influence of relativity modification mentioned above.

According to Bohr the ensemble of all components together will show no characteristic polarisation in any direction. Thus for the Stark or Zeeman effect of the hydrogen lines viewed in a direction perpendicular to that of the applied field, the sum of the intensities of the components polerized parallel to the field should equal the sum of the intensities of the components polarized perpendicular to the field.

The relative intensities as recorded by Stark[31] are in reality only relative photographic densities measured by means of a photometer. Nicholson and Merton[32] worked out the theory connecting the areas of lines obtained using a neutral wedge and the absolute relative energy content for lines of approximately the same wavelength, given by

$$\frac{E_1}{E_2} = \frac{\int I_{\lambda_1}\, d\lambda_1}{\int I_{\lambda_2}\, d\lambda_2} = \frac{\int \log_{10}^{-1} \frac{h_{\lambda_1} D_\lambda}{M}\, d\lambda_1}{\int \log_{10}^{-1} \frac{h_{\lambda_2} D_\lambda}{M}\, d\lambda_2}$$

where $\log_{10}^{-1} \frac{h_\lambda D_\lambda}{M}$ is defined as the photographic intensity of the light of wavelength λ, D is the change in density of the wedge per mm. of its length, M is the magnification, and h is the height of the line as measured on the enlargement. For lines which are close together, e.g. the Stark effect components, D_λ may be considered constant over the section considered as also may the dispersion of the spectrograph.

This method was applied by Nicholson and Merton to certain hydrogen and helium lines; but the only accurate application that has been made is in the work of Foster[32] on the helium lines λ 4922, 4472 and 4388 under the influence of steady electric fields.

III. Experimental Procedure and Results:

As a result of finding the field strength constant over the whole of the dark space near the cathode, a tube of design similar to that in Fig. IV. was made, having the slit cut shorter so that the light from the two sets of components would not overlap on the slit of the collimator tube, with a view to using it as a source in a further application of the wedge method for measuring the relative intensities for the Stark effect components of H_β and the He $\lambda 4922$ group.

Two neutral wedges, compensated by idential clear glass wedges cemented so as to make parallel plates, were mounted just in front of the collimator slit, and the light of the two polarizations was adjusted so that photographs of both could be obtained simultaneously. The space between the thin edges of the wedges was covered with black paper so that in each case the image would extend slightly past the edge thus ensuring a clear cut end to the line on the photographic plate.

The electrical outfit and vacuum system used were the same as those described in Section A, III.

Clearly the most essential requirement in using the wedge is a source which gives even illumination over the whole image. This has been effected by Foster who used only the light from a small hole in the tube very near the cathode, spreading it out into a line by the use of a sphero-cylindrical lens; but he points out that the intensity was poor and that the cathode pitting disturbed the field distribution due to the long exposures required. This source of trouble was partially eliminated by the use of the tube described above, since a great deal more light actually reached the plate, thus making the required time of exposure much less; and besides this the field distribution remained practically constant for very long exposures, since the pitting took place in a thin straight line down the centre of the cathode, the main surface of the cathode retaining its shape for some hours.

As seen from Fig. V.b. very even illumination was obtained from this type of tube as well as very good definition especially in the case of the lines appearing in the helium λ 4922 group shown. Three components on either side of the undisplaced hydrogen H line are distinguishable for both the p- and s polarizations; but as is generally the case with hydrogen, the lines are diffuse in character. Fig. V.a. is a contact print from the plate used.

Figs. VI and VII show the photographs taken with the wedges in position from which the measurements were made.

The conditions under which the plates shown were as follows:-

Fig.	Time of Exposure	Voltage across Tube	Current	H:He	Pressure in mm.Hg.	Plate No.
V	2 hrs.	9 k.v.	8 m.a.	1:2	1.3	11
VI	4½ "	8.5 "	11 "	2:1	1.6	9
VII	4 "	10.2 "	6 "	1:2	1.3	14

The main difficulties in obtaining satisfactory results lay in keeping the tube from becoming too "hard". This tendency in the tube results from the presence of the helium, the current often remaining practically constant for as long as two hours or more, and then dropping quite suddenly to two or three milli-amperes. If this occurs it is necessary to begin again, for even though sufficient light may be obtained by increasing the exposure, such a change in current is almost certain to involve some change in the character of the discharge and consequently in field strength at the point from which the light is taken. On the other hand, if a current greater than 15 or 16 milli-amperes was used initially, it was found that either the anode or cathode melted before the tube had time to become hard, and in some cases the tube cracked near the cathode due to overheating. In general the tube was cooled round the cathode section by means of a three jet air blast which could be regulated and was of some assistance in controlling the current. For the plates measured both current and voltage were very constant throughout the exposures.

The results obtained by measuring the photographs shown were calculated on the assumption that the widths of single frequency lines are the same in the vicinity of any one wavelength, and that therefore the areas of the lines must be proportional to the heights from the thin edge of the wedge to the point at which they fade away. In any case, the error in this assumption is not greater than the error involved in estimating the widths at different heights and integrating over the whole. The wedge density D was known from a previous calibration carried out by Foster, and was checked from the original plates to within one per cent by the writer, indicating the reliability of the method.

The results obtained for H_β and He λ 4922 the second term of the second subordinate series of parhelium correspond to an electric field of 44 kilovolts per cm. The H_β components are expressed relative to p: $\pm$ 10, the undisplaced line giving a direct relation between the p- and s intensities, while the helium lines are expressed relative to the 2P-4F line in the centre of the group. The diffuse doublet is separated only at the extreme end of the line where it divides, the two maxima fading away at equal rates. The relative value for p and s components was checked by means of the undisplaced lines near the helium group.

H_β - λ 4861			
p - Components		s - Components	
Z	Intensity	Z	Intensity
± 10	1	± 6	.94
± 8	1	± 4	1.5
± 6	.32	± 2	.44

He λ 4922 Group		
Line	p-Components Intensity	s - Components Intensity
2P-4P	.5) .5) Doublet	.3
2P-4F	1	.98
2P-4D	1) 1) Doublet	1.02
		.57 (Unseparated Doublet)

The helium lines 2P-4P and 2P-4F were classified by Liebert and Bohr respectively, Nyquist obtaining the first photographs in each case.

The relative intensities found in this way vary from those estimated by Stark, but not by very great amounts. The ratio of the s: = ± 4 to s: = ± 6 for H_β is clearly in total disagreement with Kramer's theory which gives the ratio 1:2, the experimental results giving it 1.6 : 1.

It is of interest to note that while the sums of the intensities in the two polarizations are not exactly equal as predicted by Bohr, the excess intensity does not exist in the same polarization for the two groups of lines studied, it being greater in the p-components for the helium group, and for the s-components in H_β. An exact balance is not to be expected from these results since all the components do not appear on the photographic plate.

The writer in conclusion wishes to express her indebtedness to the Research Council of Canada for making it possible to carry out these investigations.

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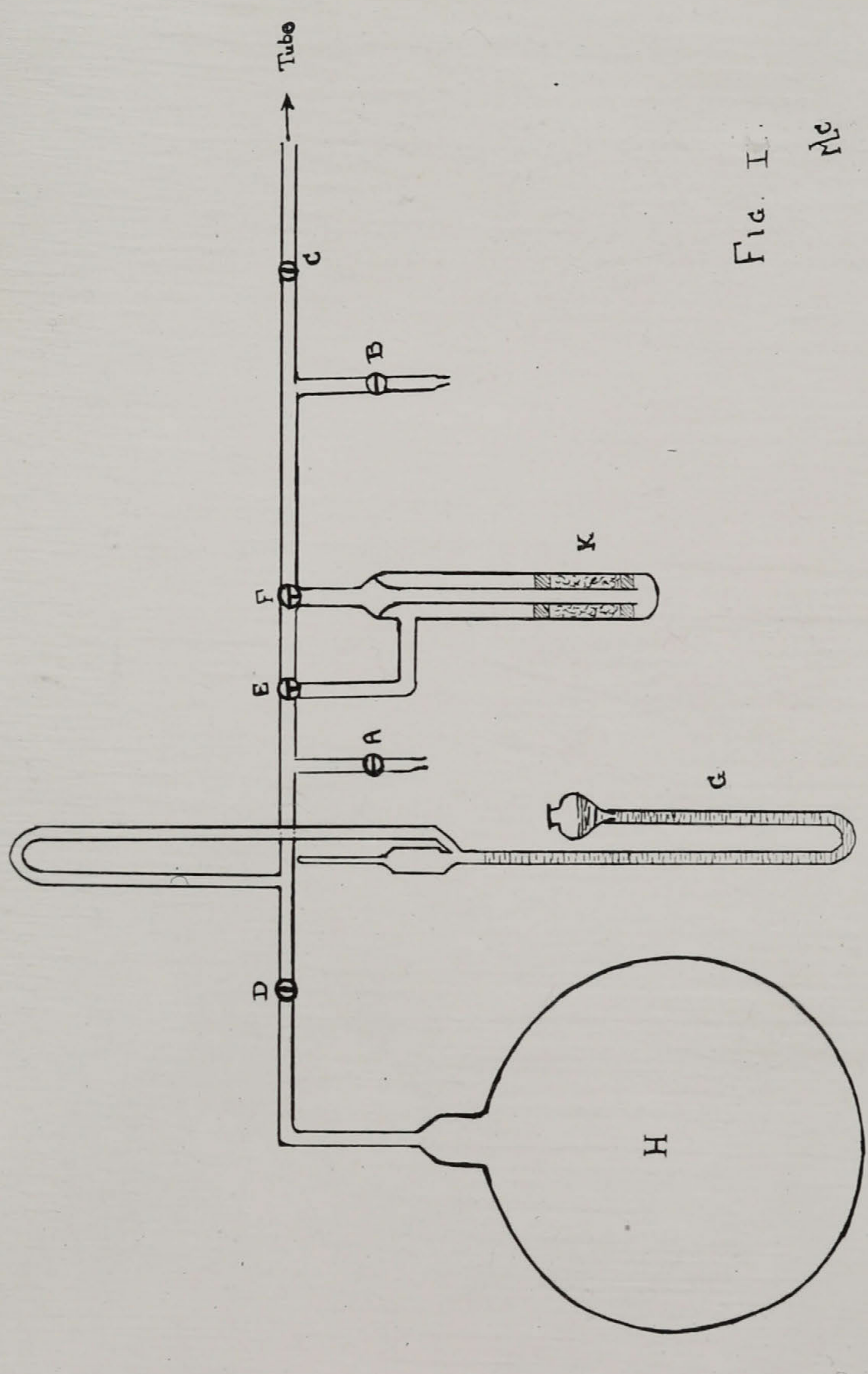

Fig. I

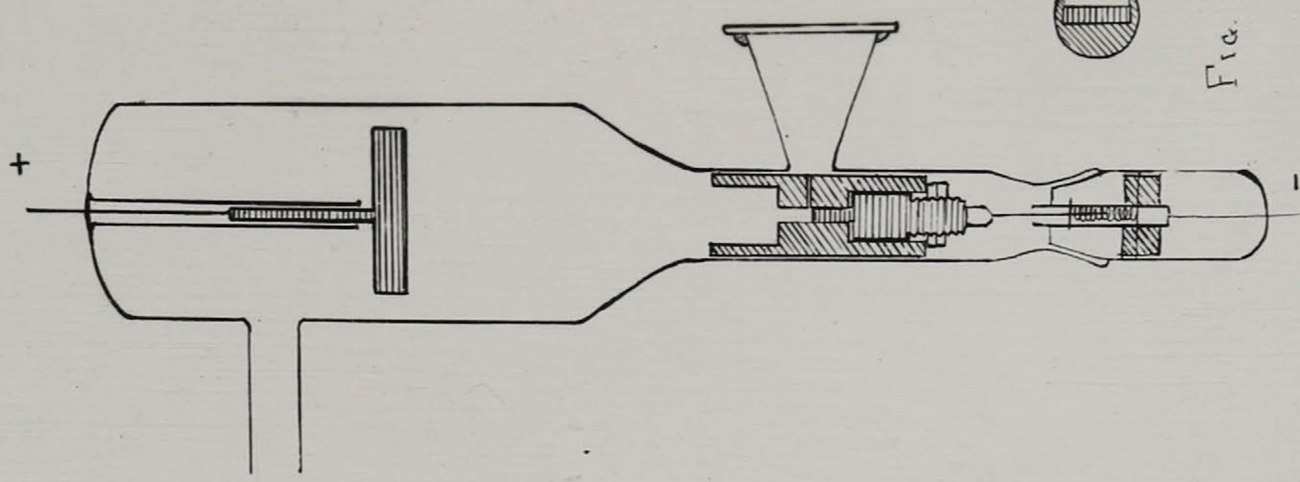

Fig. IV

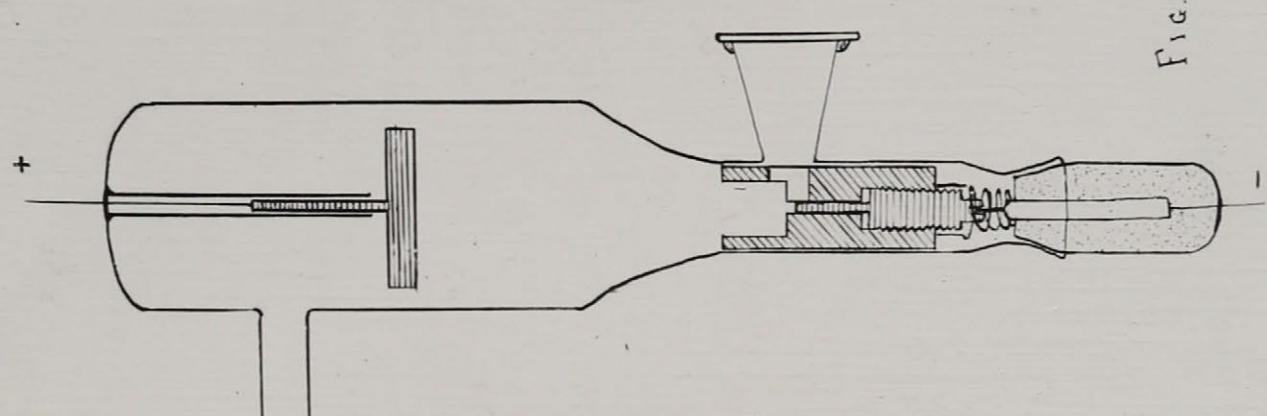

Fig. III.

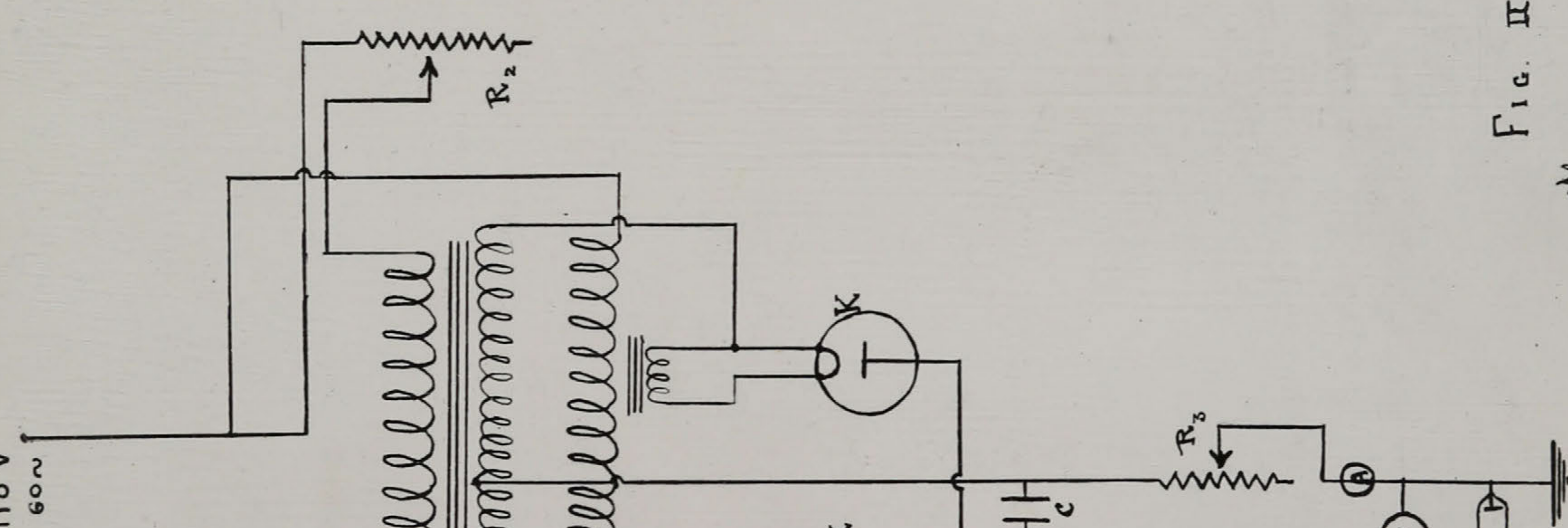

Fig. II

Fig. V. a.

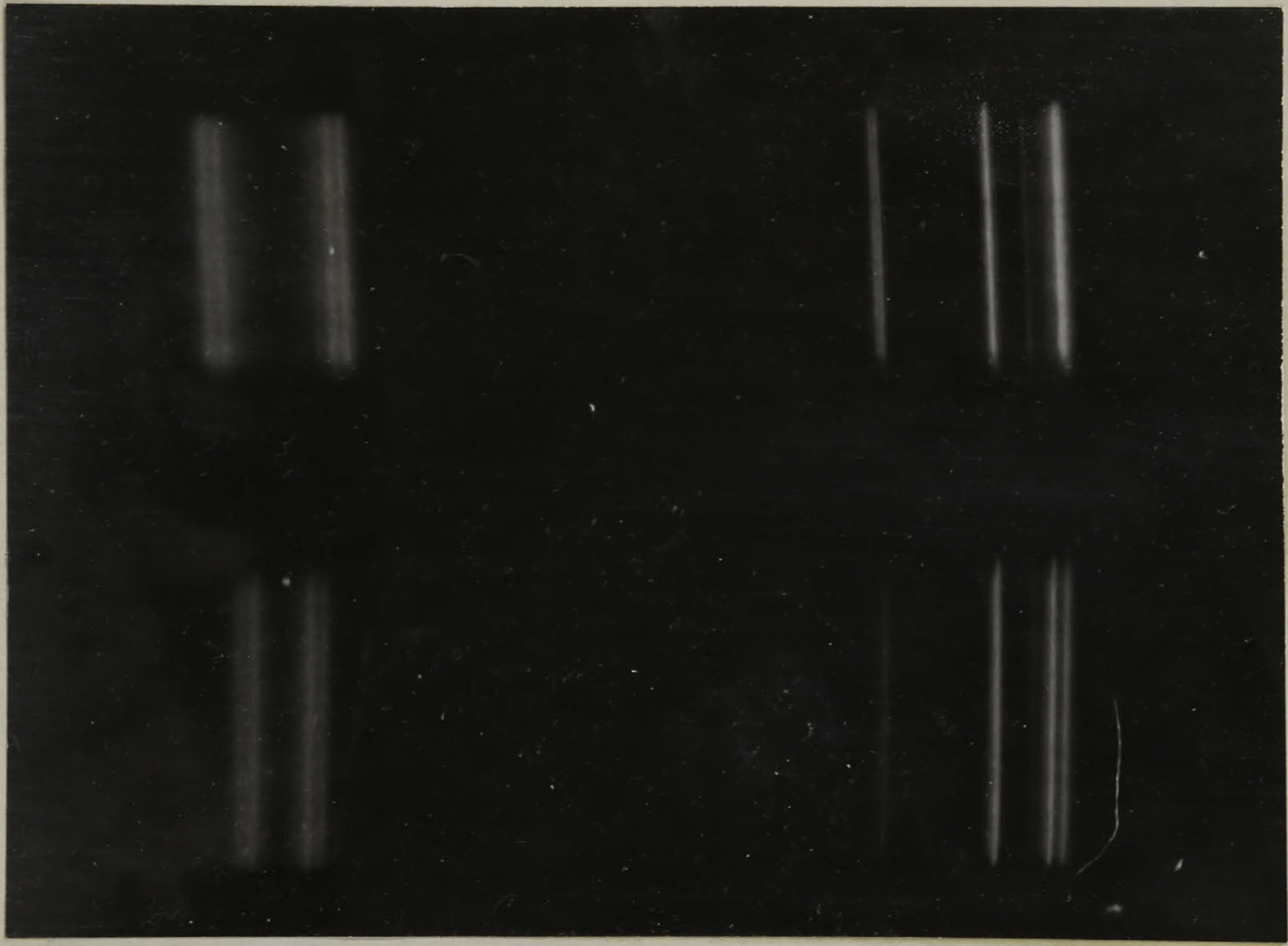

Fig. V. b.

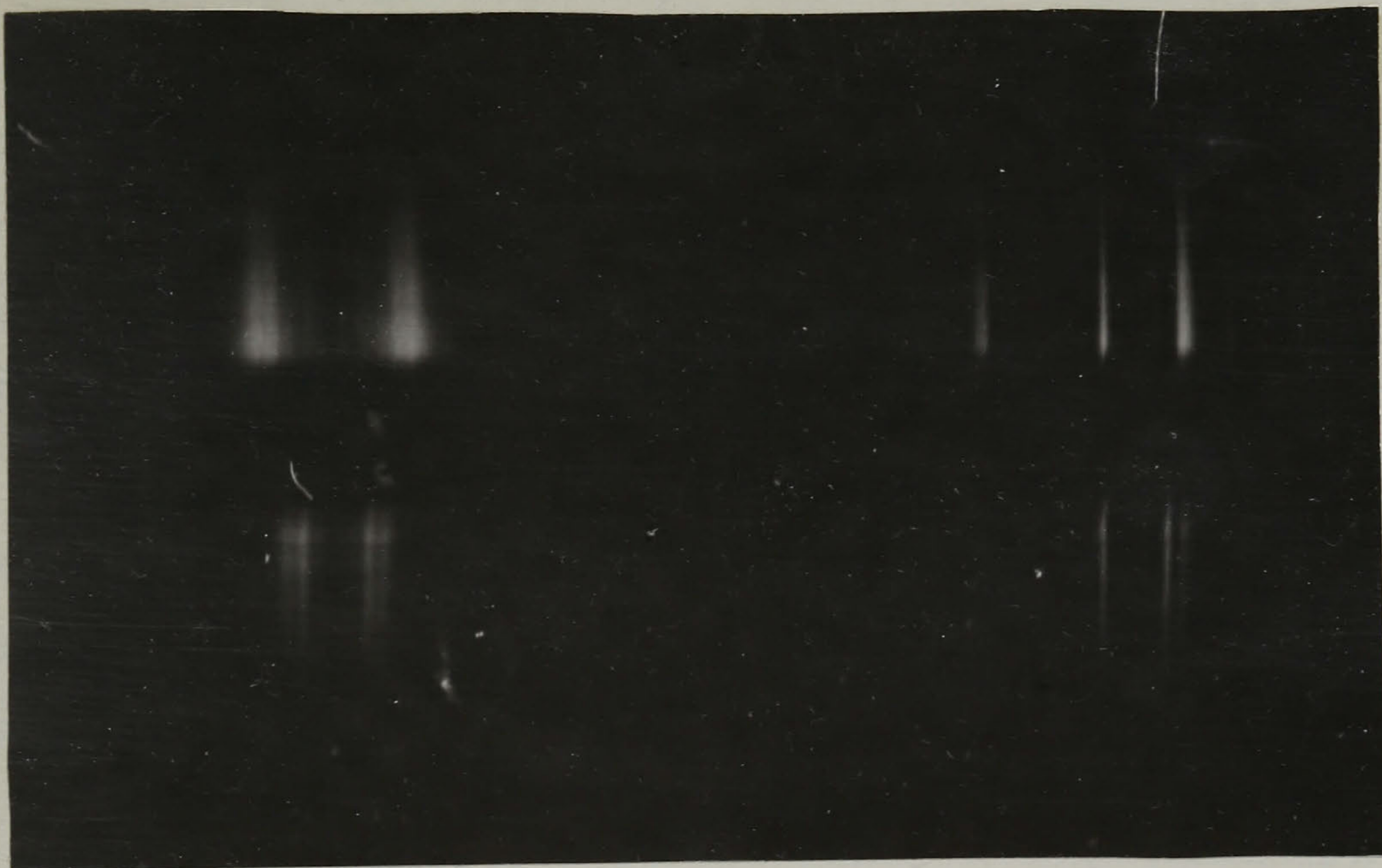

Fig. VI.

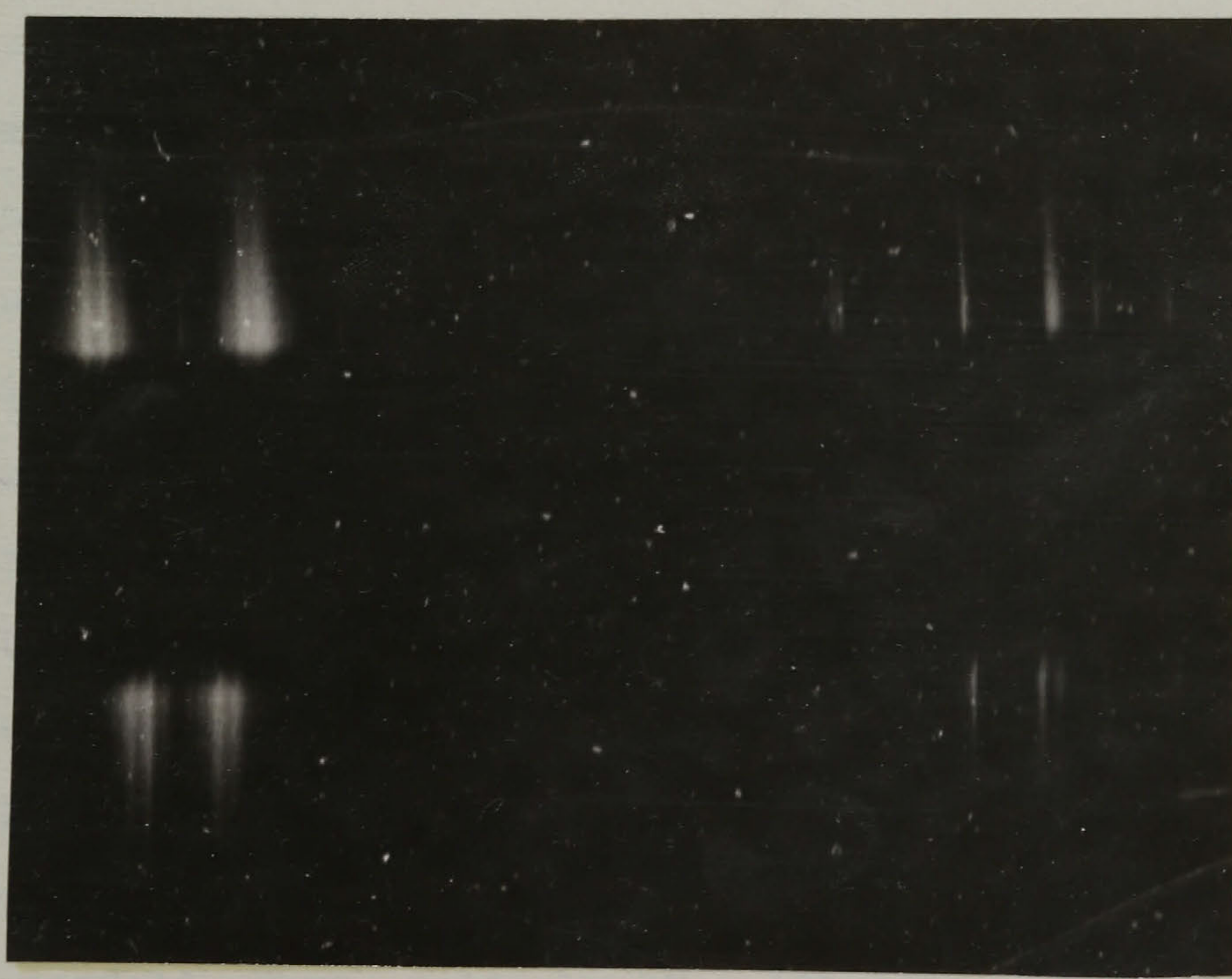

Fig. VII.

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