1953

Intensities in the hollow cathode discharge

John Philip Heller
Iowa State College

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UMI
INTENSITIES IN THE HOLLOW CATHODE DISCHARGE

by

John P. Heller

A Dissertation Submitted to the Graduate Faculty in Partial Fulfillment of The Requirements for the Degree of DOCTOR OF PHILOSOPHY

Major Subject: Physics

Approved:

Signature was redacted for privacy.

In Charge of Major Work

Signature was redacted for privacy.

Head of Major Department

Signature was redacted for privacy.

Dean of Graduate College

Iowa State College

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I. INTRODUCTION

A. Historical Description and Statement of Problem

For the examination of atomic spectra in emission, the importance of the light source is obvious. Because of this, a large part of the effort that has been expended in spectroscopy has been directed towards the development of sources with various desirable properties. Besides the refinement of flame sources, the arc has been developed into a stable as well as intense means for the excitation of relatively low lying atomic levels. Similarly, the electric spark has been transformed into a powerful tool for the production of spectral lines from highly excited and ionized states. Its high limit of excitation may be still further increased by the use of added capacity in parallel with the spark gap. In addition to the arc and spark discharges, which first distinguished between the spectra of neutral and ionized atoms for the spectroscopist, self-sustaining glow discharges at low pressures have been used as spectroscopic light sources. It may be seen, then, that the spectroscopist has of necessity become interested in the processes taking place in electrical discharges through gases and vapors.

The particular type of discharge lamp which is to be discussed here was first introduced by Paschen in 1916. Since then this hollow cathode discharge, as it is called, has been developed into an extremely useful tool of high
resolution spectroscopy. A number of reasons are responsible for this. In the first place, an early modification by Schüler\(^2\) in 1930 brought the cathode of the tube to the outside, where it could be cooled by immersion into some appropriate refrigerant. This has led to the possibility of reducing appreciably the doppler width of the observed atomic lines. A second feature of the hollow cathode discharge is that the electric field strength in the luminous region is very nearly zero. This absence of net field in the region of excitation enables the electronic transitions within the atom to take place without Stark effect, so that no line broadening effects are observed due to this cause. A further result of this low field is that ions formed in the discharge are not rapidly removed from the cathode, which makes possible the analysis of a spectrum with smaller amounts of material. Thirdly, the discharge may be maintained in a carrier gas independently of the concentration of the atoms under investigation; because of this, broadening of atomic lines caused by perturbation due to the proximity of similar atoms may also be kept down to a minimum.

In the absence of a complete description of the processes involved in the discharge, however, it is difficult to predict the effects produced by changes in the various external variables. For instance, although it has been noted by many investigators that the excitation of the atoms investigated is strongly dependent on carrier gas pressure, no
extensive data have been published on the form of this dependence.

The purpose of this investigation is to determine the empirical facts on the variation of intensity of atomic lines observed in a hollow cathode tube of typical modern form. Given these facts, it is expected that some criteria may be presented for the suitability of such a discharge tube to produce spectral lines of various types. Furthermore, it is hoped that the observed variations of intensity may lead to some further insight into the actual atomic processes involved.

B. Survey of Literature

1. The low pressure gas discharge

Inasmuch as the hollow cathode discharge is a variation of the general class of self-sustaining glow discharges, it will be helpful to examine briefly the phenomena observed in the conventional form. Here, the discharge takes place in a linear tube, between plane electrodes, in a gas pressure range from a few hundredths of a millimeter of mercury up to several centimeters. The voltage drop between anode and cathode varies with the material of the cathode and the type and pressure of gas, as well as with the physical dimensions of the tube and with the current. The appearance and characteristics of the discharge have been described by many authors. In particular, a book by K. K. Darrow\(^3\) includes photographs of such a tube at various pressures along with a rather complete description. That by von Engel and Steenbeck\(^4\) gives a...
diagram, from which Figure 1 is copied, accompanied by curves showing the variation of potential, ion concentration and other parameters along the length of the discharge. The general phenomena have also been reviewed by Druvesteyn and Penning.

It is seen from Figure 1 that the discharge is divided into several well-defined segments, which have been distinguished by more or less descriptive names. Immediately in front of the cathode is a thin region of "cathode glow", the origin of which appears to Loeb to be connected with the bombardment of the cathode by the positive ions which carry most of the current in the region. Next is the cathode dark space, in which the field strength is highest towards the cathode, and decreases with increasing distance from it. In fact, by assuming this field variation to be linear, von Engel and Steenbeck (ref. 4, p. 72) have been able to make a widely quoted analysis which yields a current voltage characteristic of the discharge that agrees with observation in the domain of abnormal discharge (i.e. at and above the point at which the cathode is fully covered with glow). The values tabulated by von Engel and Steenbeck for the thickness of the cathode, or Crookes, dark space for various combinations of gases and cathode materials have been compared by Loeb with the calculated kinetic theory mean free paths. These ratios are tabulated by Loeb (ref. 6, p. 575); their magnitudes range from 48.3 for aluminum in oxygen to 121 for iron in helium.
Figure 1  Low Pressure Discharge between Plane Electrodes

Figure 2  Low Pressure Discharge with Hollow Cathode
Therefore, it seems evident that electrons accelerated from the cathode must undergo many collisions, in the classical sense, before reaching the point of minimum field strength.

On the side away from the cathode, the Crooke dark space is bounded by the region of negative glow. Here the field strength is quite low, and the concentration of electrons is appreciable. The mean velocity of the electrons in this region is fairly high. As the concentration of electrons increases, and that of positive ions decreases towards the anode, the negative glow becomes less intense and fades gradually into the Faraday dark space. Beyond this region and filling the rest of the tube except for a small dark space in front of the anode, is the brightly glowing positive column.

Information concerning the field strengths and ion concentrations within various regions of the discharge has been obtained in several different ways. Although probe electrodes inserted into the discharge cannot be expected to assume the same potential as that region of space Nott-Smith and Langmuir have shown how their voltage-current characteristic may be used to yield both the plasma potential and the effective temperatures of the carriers. Field strength has also been measured spectroscopically by measurement of the Stark effect in various atomic spectral lines emitted from different regions of the discharge, and by the deflection of
a stream of electrons directed perpendicular to the axis of the discharge
glow discharge.

Although many modifications and refinements of the discharge tube are possible, the essential feature of the hollow cathode tube is indicated by its name. The distinguishing features of the discharge result from the geometrical shape of the cathode region, which leads to considerably higher concentrations of ions and electrons than are observed in even the positive glow portion of the usual form of glow discharge. In most investigations in which this tube has been used as a spectroscopic light source, the cathode has been cylindrical. The inside walls bounding this region constitute the cathode surface and are covered by some appropriate means with a layer of the material whose spectrum is to be examined. The shape of the anode is not critical, and may consist of a coaxial sleeve or cylinder, either surrounding the cathode or displaced some distance along their common axis. The cathode may be open at both ends, or only one. In the former case, an anode may be used at each end. A typical arrangement is shown in cross-section in Figure 2.

Under these circumstances, and within a suitable range of gas pressure, the negative glow of a discharge between anode and cathode will be concentrated inside the cathode,
separated from its interior walls by only a very narrow annular cathode dark space and cathode glow. As in a discharge in a tube with a cathode of the usual shape, the largest part of the anode-cathode potential drop takes place across this cathode dark space, and it is in this region that the electrons emitted from the cathode surface are accelerated. With the hollow form of the cathode comes the important change that this dark space becomes considerably narrower.

This effect has been studied in a somewhat similar geometry by Güntherschulze. His observations were of a discharge tube with two plane cathodes, parallel to each other and separated by a variable distance. At higher pressures these cathodes act more or less independently, each being covered with its own dark space and negative glow. As the separation of the cathodes is decreased, or as the gas pressure is reduced, the negative glows of the two cathodes overlap, but the thickness of their dark spaces decreases. As this critical separation is reached there is a large increase in the current. If the separation is decreased still further to equal the thickness of the cathode fall in a plane-electrode tube, the limiting current density for normal cathode fall exceeds by a factor of the order of one hundred that observed with the plane cathode.
The same results are observed in the cylindrical hollow cathode; the current density for normal cathode fall is greatly increased. An indication of the magnitude of the effect may be obtained from Tolansky in his rather complete discussion of the hollow cathode discharge as a source for high-resolution spectroscopy. He gives the figure 30 mA/cm² as the limiting current density in helium. The normal current density, in so-called relative units, of mA/cm² divided by the square of the gas pressure in mm of mercury, is given by Steenbeck to be $2.2 \times 10^{-3}$ for a plane iron cathode in helium. Thus, if one assumes the hollow cathode for which Tolansky quotes his value to have been of iron, and the helium to have been at the rather high pressure of about four millimeters, a current density magnification factor of one thousand is obtained. The "hollow cathode effect" has also been investigated in the cylindrical case by Lompe, Seeliger and Walter, who obtained similar results.

3. Phenomena at the cathode

The current carriers at the cathode are largely positive ions accelerated by the field in the cathode dark space and consequently having high average kinetic energy. The processes occurring at the cathode surface as a result of this ion bombardment have been studied rather extensively in many experiments. Those processes leading to the ejection of
electrons, by which the discharge is rendered self-sustaining, have been studied theoretically by Cobbs and Lamb\textsuperscript{15}, and in rather refined experiments by Regstrum\textsuperscript{16}. He bombarded molybdenum with monoenergetic helium ions, and detected a yield of about 0.2 electrons per incident He\textsuperscript{+} ion, which was roughly independent of ion energy from 0 to 1000 ev, for clean surfaces. In a gas discharge of course, the cathode surface is by no means clean, and one would expect the adsorbed gas layer to influence greatly the secondary electron emission.

A further effect of ion bombardment of the cathode, the phenomenon of sputtering, is of great importance in the use of the hollow cathode discharge as a light source. This process, by which atoms of the cathode material are introduced into the excitation region, is responsible for the possibility of using the source for the low-temperature examination of the spectra of materials with low vapor pressure. The mechanism by which an incident ion is able to eject atoms from the cathode has been suggested by von Hippel\textsuperscript{17} to be that of thermal evaporation due to the intense local heating. More recently, Keywell\textsuperscript{18} has suggested that the incident ion loses energy in successive collisions with atoms of the cathode through a diffusion process, and that each collision, until the ion has lost sufficient energy, will result in the ejection of an atom from the lattice. He, therefore, calculates on the basis of Fermi's neutron "cooling" theory,
the number of sputtered atoms per incident ion, obtaining a logarithmic dependence of this ratio on the incident ion energy. In the same letter he presents data calculated from the weight loss of a silver target bombarded by canal-ray ions from a Phillips ion gauge cathode at relatively low pressure. The numbers he obtains fit such a logarithmic curve quite well.

The majority of the investigations on the subject, however, have been concerned with the usual application of sputtering to the deposition of films on surfaces placed opposite the cathode in a discharge. Thus, C. H. Townes\textsuperscript{19}, without reference to any ejection mechanism, but accepting the experimental evidence that the sputtered particles are neutral atoms\textsuperscript{20} emitted in accord with the cosine law\textsuperscript{21}, and considering only the diffusion of the sputtered atoms, has calculated the rate of deposition in a few simple geometries. For the case in which the collector of the sputtered atoms is parallel to the cathode, Townes arrives at the conclusion that the rate of deposition should be inversely proportional to the separation between the two. This proportionality was found experimentally by Güntherschulze\textsuperscript{22} and Blechschmidt\textsuperscript{23}.

In the application of interest here, the brightness of the spectrum of the cathode material will be proportional to the concentration of sputtered atoms in the discharge region. This relationship should hold quite strictly as long as the
concentration of sputtered atoms is small compared to that of the atoms of the carrier gas.
II. EXPERIMENT

The experimental procedure was designed to yield information on the relative intensities of selected lines in the first spark spectrum of aluminum, as excited in a hollow cathode discharge with helium carrier gas. The scale of intensities was rendered uniform at all wavelengths within the range of investigation, by the use of a tungsten incandescent lamp at known temperature for plate calibration. For the purpose of surveying the general behavior of the discharge, exposures were made under a variety of conditions. The external parameters which were varied were cathode diameter, cathode temperature, total discharge current, and helium pressure. The helium used was continuously purified by circulation through appropriate traps. The wavelengths of the lines whose intensities were measured ranged from 2497 to 6182 Angstroms. This wavelength region was covered by two ten inch plates on the quartz spectrograph.

A. The Discharge Tube

Inasmuch as many of the more recent applications of the hollow cathode source have involved the spectra of relatively rare materials, low rate of consumption of the sample has become an important design feature. The operation of the discharge with very small amounts of material is made
possible by the routing of the circulating carrier gas in such a way as to provide a barrier against the escape of sputtered atoms from the cathode, and by the use of an extension of the anode to collect some of those atoms which are able to escape. The principles of such a design were laid down in 1935 by Schüler and Collnow\textsuperscript{24}. A more recent application is exemplified by a discharge tube used by Arroe and Hack\textsuperscript{25}.

For purposes of this study, an additional requirement was that of interchangeability of the cathodes. A tube was built which incorporated the above features for maximum economy of sample material and, in addition, provided for the use of various cathodes.

The discharge tube, shown in cross-section in Figure 3, was constructed of glass and metal. The upper section, of glass tubing, was wax sealed into the metal part at a tapered and ground joint. The glass tube extended upward from the taper to form the vacuum wall. It had two horizontal side tubes, near the top, and a flange at the top for a quartz window. One of the side tubes contained a tungsten wire seal for the anode lead, the other was the gas inlet. Below the taper, the glass tubing extended downward to within a centimeter of the cathode. The tapered metal member, a heavy brass ring, was soldered to a thin-walled monel tube. The lower end of this monel tube was in turn soldered to a heavy copper cylinder, which was bored to receive the actual
**Figure 3** The Experimental Tube
oathode inserts. Because of its low thermal conductivity, the monel tube made it possible to maintain the cathode and the wax seal at quite different temperatures with little heat transfer between them. A copper tube was soldered around the brass ring to keep the wax at tap water temperature. An opening was cut through the wall of the cathode block and extended into the cavity below the cathode inserts. A smaller monel tube extended upward from here to lead the gas which had circulated through the discharge back to the pump. The conical aluminum cathode inserts were bored to various internal diameters. In addition, channels were milled down their outside surfaces which connected with the discharge region through radial 1/16 inch drilled openings. Thus the circulating gas entered the discharge region, passed through these radial openings and thence down the channels between cathode and cathode block and was pumped out through the lower tube.

An anode holder, formed of sheet aluminum, extended down inside the glass tubing and was used to support anode rings, of sizes corresponding to the cathodes used. These rings served to collect some of those sputtered atoms which penetrated the "gas window" formed over the cathode. Figure 4 is a photograph showing the five cathodes used in the study, the corresponding anode rings, and the anode holder. The taper of the cathodes matched the interior taper of the
Figure 4. The cathodes, anode rings and anode holder.

Figure 5. The experimental tube.
cathode block quite closely to guarantee good thermal contact between the two. The assembled tube is shown in operation in Figure 5, with the cathode immersed in a beaker of water for temperature control.

The gas circulating system was of standard form, and utilized a glass mercury pump with especially small diameter jet. From the high pressure side of the pump, the helium passed in succession through an oven containing cuprous oxide for removal of hydrogen, a cold trap containing charcoal, past a small tilting McLeod gauge, through a cold trap and into the top of the discharge tube. From the bottom of the cathode block in the discharge tube the helium was led through another cold trap and back to the mercury pump. The circulating system, with associated details, is shown in Figure 6. It was found, occasionally, that after the system had been opened to the atmosphere mercury from the McLeod gauge had condensed in the connecting tubes on either side of the discharge tube, between the liquid air traps. To speed the removal of any mercury contamination here, these connecting tubes were wrapped with asbestos tape and heater winding to maintain them at about 100°C. For use with helium as a carrier gas, all cold traps were immersed in liquid nitrogen. The circulating system which was built for this investigation also had an alternative path for the use of argon as a carrier gas. The argon could be purified by circulating it through a discharge between magnesium electrodes instead of
Figure 6  The Circulating System
The hollow cathode discharge received power from a 2.00 volt D.C. generator, through a bank of ten 75 watt light bulbs in series to act as ballast. The output was controlled by rheostats in the field circuit of the generator, power for field coils being obtained from the 115 volt A.C. supply.

In operation, the discharge was in general more stable at higher pressures, with larger cathodes, at lower currents and at lower temperatures. However, the region of instability overlapped the planned range of operating conditions only for the smallest cathode diameter, at the lower pressures. Thus it was found impossible, with the 3.5 mm cathode at 100°C., to keep the discharge inside the cathode for pressures less than 2 mm. Even with this cathode at ice temperature, when the pressure could be reduced to 1.05 mm, the maximum current possible was only about half that used for the other high-current exposures. The voltage across the tube for a given current increased rather slowly with decreasing pressure until the region of instability was approached, when it rose fairly rapidly.

The purification of the helium was principally accomplished by the adsorption of foreign gases in the activated charcoal. The charcoal trap was immersed in liquid nitrogen, and proved quite effective. To maintain the adsorption capacity, the general operating procedure adopted included baking the trap at about 450°C. overnight with the forepump.
on, after each day's exposures. In the morning the oven was removed, and after cooling, the charcoal trap was again ready for use.

B. The Calibration Source

For calibration purposes, a special incandescent lamp was constructed with a quartz end, joined to a pyrex body with a graded seal. The leads were brought into the tube by means of two Kovar-to-glass tube seals, and the filament, a tungsten ribbon .040 by .008 inches, by about 5/8 inch long, was spot-welded onto heavy nickel leads. The upper part of the tube contained a ring-shaped tray of calcium metal. The tube was filled through a one centimeter bore pyrex stopcock, which was also used for sealing off. The cleaning and filling procedure finally adopted involved a thorough evacuation with a mercury diffusion pump through a cold trap, and baking at 450°C. After the baking had been in progress for two or three hours to ensure the decomposition of any calcium hydroxide on the surface of the calcium chips, the oven was removed and the tray of calcium heated by induction to a bright red. This vaporized the calcium metal, which condensed onto the upper part of the tube. The oven was then replaced and baking continued for two more hours. The tube was then slowly filled with commercial argon, through a U tube trap in liquid oxygen to freeze out any water vapor.
contamination. Oxygen, rather than nitrogen, was used on the cold trap to avoid excessive condensation of the argon gas. The argon pressure inside the tube was brought up to about two atmospheres and the stopcock closed. The lamp was then ready for use.

The filament of the lamp was run at a brightness temperature of 2400°C, as measured on a Leeds and Northrup optical pyrometer. This corresponds to an actual temperature of 3600°K. The relative energy output of a black body at this temperature was calculated as a function of wavelength using Wien's approximation and these figures were multiplied by the emissivity of tungsten at this temperature and at the appropriate wavelength. The emissivity values used were graphically interpolated from data published by Hemker. At the operating temperature, the total power dissipation of the lamp was about 65 watts. The lamp was operated from the D.C. supply, with storage batteries in parallel for regulation, and a balancing resistor set so that the rate of discharge of the batteries was approximately zero.

The object of the argon filling of the lamp was to retard evaporation of the tungsten. Despite this, the filament ribbon evidently did decrease in thickness during the course of the experiment. The small progressive increase in resistance noted was, at the time of the exposures, erroneously attributed to trouble with the lead wires, and consequently,
the lamp was set each time at the current which had raised the filament to the proper temperature when it was first calibrated. Upon the completion of the series of exposures, the temperature was again measured at this current and it was discovered that the increase of resistance had been primarily due to evaporation of filament material.

A set of correction factors was calculated to fit the observed data on the voltage required by the lamp during the course of its use. The temperature increase predicted from this calculation matched that observed at the conclusion of the series of exposures quite closely. These corrections were, therefore, applied with confidence in the final reduction of data as described below.

C. The Spectrograph and Optical System

The spectrograph used was a single prism instrument, with focal length of the camera lens longer than that of the collimator lens, modeled after the Bausch and Lomb medium quartz spectrograph. The radiation which emerged from the discharge tube passed through a quartz lens of 12 cm focal length, was turned through 90° by an aluminized front surface mirror, and formed an image of the cathode 12 cm in front of the spectrograph slit. This image was in turn focused on the collimator lens of the spectrograph by a quartz condensing lens of focal length 8.1 cm, which was placed 2.5 cm in
Figure 7  The Optical Arrangement
front of the slit. The magnification obtained with this optical train was such that the collimator lens was just filled with light when the smallest cathode (3.5 mm diameter opening) was used. With larger cathode sizes, of course, only light from their centers was utilized by the spectrometer. Because of this situation, the data as obtained compare the average brightnesses of the discharges.

For comparison of the hollow cathode source with the tungsten lamp, the mounting of the latter was pivoted to permit its filament to occupy the same position in front of the condensing lens as the first image of the hollow cathode. With the calibration source in place, an enlarged image of its filament was projected onto the collimator lens. This image extended horizontally across the collimator and was 5.2 mm high. Figure 7 is a diagram of the optical system. For use with the calibration lamp, a symmetrical, five step sector wheel between the condensing lens and slit was rotated at 3600 r.p.m. With two periods of the step pattern around the circumference of the sector wheel, the resulting frequency of 120 flashes per second is safely above the rates at which the response of the photographic emulsion is distorted by the intermittency effect.

The comparison of radiant energy in continuous and in line spectra involves some of the constants of the dispersing system. If $E_\lambda$ ergs/cm²/sec is the radiant energy flux density from a monochromatic source of wavelength $\lambda$, incident on the
slit within the solid angle accepted by the collimator, then the energy flux transmitted by the spectrograph is 
\[ \varepsilon_{\lambda} \cdot \text{lwf} \text{ ergs/sec} \]. Here \( l \) and \( w \) are the length and width of the slit, and \( f \) the transmission factor of the spectrograph optics. This radiation is focused onto the plate to form an image of the slit \( l' \) cm high and \( w' \) cm wide. The energy flux density on the plate at position \( s \), corresponding to the wavelength \( \lambda \) is then \( \varepsilon_{\lambda} \cdot \text{flw}/l'w' \) ergs/cm\(^2\)sec. For line spectra which do not overlap, the dispersion of the prism has no effect so long as the width of the spectral line is small enough so that its dispersed image is small compared to the geometrical slit image width \( w' \).

For a continuous spectrum, however, the dispersion of the prism becomes important. In this case the energy density at the wavelength \( \lambda \) within a wavelength range \( d\lambda \) must be written \( J_{\lambda} d\lambda \), again in ergs/cm\(^2\)sec. The resultant energy flux density on the plate at position \( s \) is \( J_{\lambda} d\lambda \cdot \text{flw}/l'w' \) ergs/cm\(^2\)sec. At the position \( s \), however, the plate receives light of wavelengths different from \( \lambda \) due to the continuous overlap of the slit images. To calculate the total energy flux density incident on the plate one must integrate the above expression over the range of wavelength falling on the plate at this point. The extent of this range is determined by the width of the spectrograph slit, so that the total energy flux density at point \( s \) is:
The ratio of the energy flux densities at the plate from a continuous source and from a line source is therefore:

\[ \frac{J_\lambda}{E} \frac{d\lambda}{ds} \cdot \frac{w}{M_w} \]

where \( M_w \) is the horizontal magnification of the slit image in the spectrograph. Both \( M_w \) and \( \frac{d\lambda}{ds} \) vary with wavelength.

In accord with these results, the calculated energy flux from the tungsten lamp was multiplied by the linear dispersion of the spectrograph, its horizontal magnification, and the slit width. This function was then taken as proportional to the energy flux density incident on the plate at various wavelengths from the calibration lamp.

The spectra were recorded on two different kinds of photographic emulsion. For the wavelength range 2490 to 3100 Angstroms, Eastman type S4 1 plates were used. This emulsion is not especially sensitized beyond the natural wavelength range of silver bromide, and was used in the ultraviolet exposures to minimize fogging from the rather intense light of longer wavelengths, which was scattered from the optics during the calibration exposures. In the near ultraviolet and visible region, Eastman type N plates were used. The
effect of scattered light was negligible here, due to the shorter calibration exposures necessary at these longer wavelengths. The plates were developed in DX 50, as uniformly as possible by hand, and with constant brushing to minimize the Eberhard effect\textsuperscript{29} in the neighborhood of the calibration strips.

D. The Plan of Exposure

With each of the five cathodes a pair of plates was exposed at each of three different cathode temperatures. These were determined by appropriate constant temperature baths, into which the lower end of the tube was immersed. Liquid nitrogen, ice and water, and boiling water were used. On each plate, in addition to the calibration spectra, exposures to the hollow cathode discharge were made at four different carrier gas pressures. In all cases except that with the smallest diameter cathode, the pressures at which exposures were made were 6.0, 4.0, 2.00 and 1.00 mm of mercury. At each of these pressures, an exposure was made at high current (about 650 ma total discharge current) and at low current (about 200 ma). In addition, the plates exposed with the largest cathode also contained spectra at an intermediate current. On the remaining plates, two high current spectra were recorded at each pressure. These differed in exposure time by a factor of ten. Thus each plate contained
twelve atomic spectra. These spectra contained many lines of He I, some of He II, the stronger lines of Al I and II, and some impurity lines. These latter included the sensitive lines of magnesium in the green, Mg I λ2556, and, occasionally, Mg I λ5461.

From among these, twenty-eight lines from the spectra of singly ionized aluminum were selected for study. These included all detectable members of three series, the \(3^{2}D - n^{2}F\), the \(4^{3}D - n^{3}F\) and the \(4^{3}F - n^{3}G\). In addition, three lines originating from low-lying Al II levels were measured. This yielded information on the total rate of excitation of ionized aluminum to singlet and triplet states.

2. The reduction of data

The light transmitted by the plates at wave-lengths of interest was measured on an Applied Research Laboratories microphotometer-comparator. The lines whose intensities were to be measured were first identified on one pair of plates, upon which the positions of all lines had been measured with an erlikon comparator. From the data on these plates, and with the use of appropriately spaced helium lines as standards, the Hartmann dispersion formula was used to calculate the wavelengths of all lines. After drawing correction curves to further verify the identification of the selected aluminum II lines, these were marked with ink dots.
The dots were transferred to the other plates and, as a further check, maps were drawn of the images of these and surrounding lines as they appeared on the Applied Research Laboratories comparator screen. The photo-electric cell galvanometer circuit of this instrument was set to read 100 at a clear portion of each plate which had been shielded from exposure by the side of the plateholder. In addition to the readings of transmission at each step of the continuous spectra at the selected wavelengths, and of the lines themselves on the discharge tube spectra, background readings were taken on either side of the lines.

The resultant galvanometer readings were reduced to intensity values by the use of characteristic curves, of log galvanometer reading against log exposure. These characteristic curves were plotted from the galvanometer readings of the calibration spectra. It was found that development conditions of all the plates had been very nearly equal, so that the slopes of sample characteristic curves varied little from plate to plate. Accordingly, a set of "master curves", one for each wavelength, was plotted from plates of average contrast. Linear correction curves were then drawn on tracing paper for each plate, their slopes representing the relative deviation of the contrast of that plate from the mean. The net exposure (i.e. a number proportional to the line's original energy density on the plate), was then determined graphically as the difference in exposure between the line
and its background. The correction for the slope of the characteristic curves was accomplished by use of the tracing paper overlay, and the additional correction for the aging of the tungsten calibration source was applied by shifting the overlay the calculated distance along the exposure ordinate of the log-log paper on which the master curve was drawn.

These values were then divided by the time of exposure to give a new set of numbers, proportional to the brightness of the source at each of the selected wavelengths.
III. RESULTS

A. Presentation of Data

The brightnesses of all lines measured are given on an arbitrary scale. With exposures of ten minutes, the lowest brightness measurable on the plates was about 3.05 in these units. The numerical data on the brightness of the source at the various wavelengths is presented in two parts.

The results for members of the three series of lines are given graphically. Each graph shows line brightness as a function of the principal quantum number n of the level from which the line originates. The abscissa is drawn to a linear scale, giving the excitation energy of the upper level. This scale is in units of reciprocal centimeters above the ground state of neutral aluminum.

Several points are to be noted, in general, concerning all the charts. Although the same unit of brightness is retained throughout, two different scales are utilized for the ordinate. Thus, the charts of data taken at high discharge current have an ordinate scale of 5 brightness units per inch, while the low current data is plotted at 2 1/2 units per inch.

Inasmuch as it is the source brightness which is given below, it must be remembered that the data do not directly represent the effect of varying cathode size on the total
radiated power. The observed brightness from the smaller cathodes is further accentuated because the discharge currents were roughly the same for all cathodes.

The data on the series lines have been presented graphically in order to display, more conveniently, the changes in line brightness from one series member to the next, and to show how these relationships vary with the external parameters of the discharge.

The strength of all Al II lines was dependent also on the efficiency of sputtering and of ionization of the aluminum atoms. Independent information on the concentration of aluminum was obtained from measurements of source brightness at the wavelengths of three transitions from low-lying levels. To yield data on the excitation to singlet Al II levels, the two transitions \(3^1P - 4^1S\) and \(3^1P - 3^2P^2^1D\), at 2816 and 3901 respectively, were observed. To determine the degree of triplet excitation, the inter-combination line \(3^1S_0 - 3^3P_1\) at 2669 was measured. These brightnesses, in the same units as used above, are presented in tabular form following the graphs of the series data.

All of the high current exposures except two were with 650 ma discharge current. In all data pertaining to the 3.50 mm cathode, the current was 365 ma for the exposures at 1.05 mm, and 550 ma for those at 2.00 mm.

The low current data were taken with various discharge current values, shown in Table 5.
**Figure 8. Singlet F Series at High Current**

(Variation of Brightness with Carrier Gas Pressure and Cathode Diameter)

The members of the series $3^1D - n^1F$, with their wavelengths and excitation energies, are:

<table>
<thead>
<tr>
<th>n</th>
<th>$\lambda$</th>
<th>$E$ above $Al I $ ground state $\text{cm}^{-1}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>6</td>
<td>3428.9 Å</td>
<td>187,522.1</td>
</tr>
<tr>
<td>7</td>
<td>3074.7</td>
<td>190,880.8</td>
</tr>
<tr>
<td>8</td>
<td>2881.5</td>
<td>193,061.1</td>
</tr>
<tr>
<td>9</td>
<td>2762.5</td>
<td>194,555.7</td>
</tr>
<tr>
<td>10</td>
<td>2663.3</td>
<td>195,623.4</td>
</tr>
<tr>
<td>11</td>
<td>2627.7</td>
<td>196,411.8</td>
</tr>
<tr>
<td>12</td>
<td>2586.9</td>
<td>197,010.8</td>
</tr>
<tr>
<td>13</td>
<td>2556.0</td>
<td>197,478.4</td>
</tr>
<tr>
<td>14</td>
<td>2532.1</td>
<td>197,847.8</td>
</tr>
<tr>
<td>15</td>
<td>2513.15</td>
<td>198,145.4</td>
</tr>
<tr>
<td>16</td>
<td>2497.85</td>
<td>198,388.9</td>
</tr>
</tbody>
</table>

Cathode temperature for all of the graphs in this figure was $0^\circ\text{C}$. 
Brightness

Cathode Diam. = 10.5 mm.

Cathode Diam. = 14.0 mm.
Figure 8 Singlet F Series at High Current
Figure 9. Singlet F Series at Low Current

(Variation of Brightness with Carrier Gas Pressure and Cathode Diameter, at Low Current)

Cathode temperature for all of the graphs in this figure was 0°C.
Cathode Diam.= 10.5 mm.

Cathode Diam.= 14.0 mm.
Quantum Number $n$ of Higher Excited State

Excitation Energy Above Ground State of AI I, in thousands of cm$^{-1}$

Figure 9 Singlet F Series at Low Current
Figure 10. Singlet F Series - High Current

(Variation of Brightness with Carrier Gas Pressure and Cathode Temperature at High Current)

Cathode diameter for all of the graphs in this figure was 7.24 mm.

The graphs at $T_{cath} = 0^\circ C$ are duplicates of the graphs at cathode diameter 7.24 mm in Figure 8.
Cathode Temp. = 100°C
Cathode Temp. = 0°C
Figure 10  Singlet F Series at High Current
Cathode diameter for all graphs in this figure was 7.24 mm.

The graphs at $T_{\text{cath}} = 0^\circ\text{C.}$ are duplicates of the graphs at cathode diameter 7.24 mm in Figure 9.
Quantum Number $\ell$ of Higher Excited State

Excitation Energy Above Ground State of Al I, in thousands of cm$^{-1}$

Figure II: Singlet F Series at Low Current
The members of the series $4s^3P - n^3F$, with their wavelengths and excitation energies, are:

<table>
<thead>
<tr>
<th>n</th>
<th>$\lambda$ (Å)</th>
<th>$E$ above Al I ground state (cm$^{-1}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>7</td>
<td>4586</td>
<td>191,549.0</td>
</tr>
<tr>
<td>8</td>
<td>4227</td>
<td>193,408.1</td>
</tr>
<tr>
<td>9</td>
<td>3996</td>
<td>194,777.0</td>
</tr>
<tr>
<td>10</td>
<td>3842</td>
<td>195,779.4</td>
</tr>
<tr>
<td>11</td>
<td>3734</td>
<td>196,528.3</td>
</tr>
<tr>
<td>12</td>
<td>3656</td>
<td>197,101.7</td>
</tr>
<tr>
<td>13</td>
<td>3597</td>
<td>197,548.7</td>
</tr>
<tr>
<td>14</td>
<td>3552</td>
<td>197,904.7</td>
</tr>
<tr>
<td>15</td>
<td>3516</td>
<td>198,192.4</td>
</tr>
</tbody>
</table>

The twelfth member of this series, $\lambda 3656$, was not observable here because of interference from the much stronger Al II line, $4s^3\Sigma_2 - 5s^3D_3$ at $\lambda 3655$.

Measurements were not possible in all cases on the tenth series member, $\lambda 3842$, due to the high background from halation on the plot in the neighborhood of the helium line at $\lambda 3838$.

Cathode temperature for all of the graphs in this figure was 0°C.
Figure 12 Triplet F Series at High Current
Figure 13. **Triplet F Series - Low Current**

(Variation of Brightness with Carrier Gas Pressure and Cathode Diameter at Low Current)

Cathode temperature for all of the graphs in this figure was 0°C.
Cathode Diam. = 10.5 mm

Cathode Diam. = 14.0 mm
Figure 13 Triplet F Series at Low Current

Cathode Diam. = 14.0 mm

Cathode Diam. = 17.7 mm

Quantum Number Π of Higher Excited State

Excitation Energy Above Ground State of Al I, in thousands of cm⁻¹
Figure 14. Triplet F Series - High Current

(Variation of Brightness with Carrier Gas Pressure and Cathode Temperature at High Current)

Cathode diameter for all of the graphs in this figure was 7.24 mm.

The graphs at $T_{\text{Cath}} = 0^\circ\text{C.}$ are duplicates of the graphs at cathode diameter 7.24 mm in Figure 12.
Cathode Temp. = 0°C

Cathode Temp. = 100°C
Cothode Temp. = -190°C

P in mm Hg

0.00

2.00

4.0

6.0

Figure 14 Triplet F Series at High Current
Figure 15. Triplet F Series - Low Current

(Variation of Brightness with Carrier Gas Pressure and Cathode Temperature at Low Current)

Cathode diameter for all of the graphs in this figure was 7.24 mm.

The graphs at $T_{\text{cath}} = 0^\circ\text{C.}$ are duplicates of the graphs at cathode diameter 7.24 mm in Figure 13.
Figure 15 Triplet F Series at Low Current

Cathode Temp. = -190°C

Brightness

Quantum Number $n$ of Higher Excited State

Excitation Energy Above Ground State of Al I, in thousands of cm$^{-1}$

$P$ in mm Hg

1.00

2.00

4.0

6.0
The members of the series $4^3F - n^3G$, with their wavelengths and excitation energies, are:

<table>
<thead>
<tr>
<th>n</th>
<th>$\lambda$</th>
<th>$E_{\text{above } \lambda}$</th>
<th>$I$</th>
<th>ground state</th>
</tr>
</thead>
<tbody>
<tr>
<td>6</td>
<td>6182 Å</td>
<td>187,867.9 cm$^{-1}$</td>
<td></td>
<td></td>
</tr>
<tr>
<td>7</td>
<td>5145</td>
<td>191,128.4</td>
<td></td>
<td></td>
</tr>
<tr>
<td>8</td>
<td>4640</td>
<td>193,243.9</td>
<td></td>
<td></td>
</tr>
<tr>
<td>9</td>
<td>4347</td>
<td>194,693.7</td>
<td></td>
<td></td>
</tr>
<tr>
<td>10</td>
<td>4160</td>
<td>195,730.2</td>
<td></td>
<td></td>
</tr>
<tr>
<td>11</td>
<td>4031</td>
<td>196,496.8</td>
<td></td>
<td></td>
</tr>
<tr>
<td>12</td>
<td>3939</td>
<td>197,079.6</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Uncertainties on the 11th series member, $\lambda_{4031}$, were large due to the high background from halation surrounding the very strong helium line $\lambda_{4026}$. These errors are indicated by vertical lines through the points.

The 9th series member, $\lambda_{4347}$, was masked in one case by interference from a close impurity line.

Cathode temperature for all of the graphs in this figure was 0°C.
Quantum Number $\ell$ of Higher Excited State

Excitation Energy Above Ground State of Al I, in thousands of cm$^{-1}$

Figure 16: Triplet G Series at High Current
Cathode temperature for all of the graphs in this figure was 0°C.
Cathode Diam.= 14.0 mm

Cathode Diam.= 17.7 mm

Quantum Number $\ell$ of Higher Excited State

Excitation Energy Above Ground State of Al I, in thousands of cm$^{-1}$

Figure 17. Triplet G Series at Low Current
Figure 18  

Triplet G Series - High Current

(Variation of Brightness with Carrier Gas Pressure and Cathode Temperature at High Current)

Cathode diameter for all of the graphs in this figure was 7.24 mm.

The graphs at $T_{\text{cath}} = 0^\circ$ C. are duplicates of the graphs at cathode diameter 7.24 mm in Figure 16.
Cathode Temp. = -190°C

Figure 18 Triplet G Series at High Current
Figure 19. Triplet G Series - Low Current

(Variation of Brightness with Carrier Gas Pressure and Cathode Temperature at Low Current)

Cathode diameter for all of the graphs in this figure was 7.24 mm.

The graphs at $T_{\text{cath}} = 0^\circ\text{C.}$ are duplicates of the graphs at cathode diameter 7.24 mm in Figure 17.
Figure 19 Triplet G Series at Low Current

Cathode Temp. = 190°C

- Brightness

Quantum Number $N$ of Higher Excited State

Excitation Energy Above Ground State of Al I, in thousands of cm$^{-1}$
Table 1

Brightness of Lines from Low Al II Levels at Varying Cathode Diameters and Helium Pressures with High Current, Cathode at 0°C.

<table>
<thead>
<tr>
<th>p mm Hg</th>
<th>3.50mm</th>
<th>7.24mm</th>
<th>10.5mm</th>
<th>14.0mm</th>
<th>17.7mm</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.00</td>
<td>1300</td>
<td>500</td>
<td>500</td>
<td>900</td>
<td>900</td>
</tr>
<tr>
<td></td>
<td>49</td>
<td>105</td>
<td>53</td>
<td>200</td>
<td>21</td>
</tr>
<tr>
<td></td>
<td>20 ± 2</td>
<td>16 ± 1</td>
<td>27</td>
<td>33</td>
<td>14.8</td>
</tr>
<tr>
<td>2.00</td>
<td>1300</td>
<td>500</td>
<td>330</td>
<td>420</td>
<td>45</td>
</tr>
<tr>
<td></td>
<td>90</td>
<td>70 ± 5</td>
<td>16</td>
<td>35</td>
<td>2.8</td>
</tr>
<tr>
<td></td>
<td>31 ± 3</td>
<td>19</td>
<td>10.5</td>
<td>11 ± 1</td>
<td>2.6</td>
</tr>
<tr>
<td>4.0</td>
<td>1300</td>
<td>350</td>
<td>210</td>
<td>290</td>
<td>135 ± 10</td>
</tr>
<tr>
<td></td>
<td>62</td>
<td>19</td>
<td>5.0</td>
<td>8.5 ± 8</td>
<td>2.3</td>
</tr>
<tr>
<td></td>
<td>30 ± 3</td>
<td>6.4</td>
<td>3.2</td>
<td>3.1 ± 5</td>
<td>1.65</td>
</tr>
<tr>
<td>6.0</td>
<td>760 ± 80</td>
<td>230 ± 23</td>
<td>200 ± 20</td>
<td>220 ± 22</td>
<td>33</td>
</tr>
<tr>
<td></td>
<td>18.4</td>
<td>8.5</td>
<td>2.7</td>
<td>4.9</td>
<td>2.1</td>
</tr>
<tr>
<td></td>
<td>20 ± 2</td>
<td>3.5 ± 4</td>
<td>2.0</td>
<td>2.0</td>
<td>0.2 ± 05</td>
</tr>
</tbody>
</table>

* Each entry in the tables consists of three numbers arranged vertically; these numbers give the brightnesses of the lines λ2816, λ3901 and λ2669 respectively. The first two of these are lines from singlet levels, the third is an intercombination line from the lowest triplet level. The entries in the succeeding tables are also arranged in this order.

* The helium pressure was adjusted at 1.05mm instead of 1.00mm for this 3.50mm cathode for the sake of stability.

* The helium pressure during the exposures with the 14.0 mm cathode was 0.95mm instead of 1.00mm.
Table 2

Brightness of Lines from Low Al II Levels at Varying Cathode Diameters and Helium Pressures with Low Current, Cathode at 0°C.

<table>
<thead>
<tr>
<th>p (mm Hg)</th>
<th>3.50mm</th>
<th>7.24mm</th>
<th>10.5mm</th>
<th>14.0mm</th>
<th>17.7mm</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.00</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>&gt;</td>
<td>71^a</td>
<td>92</td>
<td>110±11</td>
<td>96±9^b</td>
<td>7.8</td>
</tr>
<tr>
<td></td>
<td>11.1^a</td>
<td>37</td>
<td>19</td>
<td>47±4^b</td>
<td>2.34</td>
</tr>
<tr>
<td></td>
<td>2.45^a</td>
<td>3.0</td>
<td>6.3</td>
<td>7.1</td>
<td>1.63</td>
</tr>
<tr>
<td>2.00</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>&gt;</td>
<td>86</td>
<td>150±15</td>
<td>66±7</td>
<td>30</td>
<td>4.5</td>
</tr>
<tr>
<td></td>
<td>11.3</td>
<td>23</td>
<td>5.1</td>
<td>7.2</td>
<td>0.35</td>
</tr>
<tr>
<td></td>
<td>3.1</td>
<td>3.6</td>
<td>3.7</td>
<td>1.8</td>
<td>0.26</td>
</tr>
<tr>
<td>4.0</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>110±11</td>
<td>23</td>
<td>13.4</td>
<td>33</td>
<td>2.61</td>
</tr>
<tr>
<td></td>
<td>4.3</td>
<td>3.4</td>
<td>0.59</td>
<td>1.05</td>
<td>0.04±0.1</td>
</tr>
<tr>
<td></td>
<td>1.65</td>
<td>0.94</td>
<td>0.30</td>
<td>0.56</td>
<td>0.04±0.1</td>
</tr>
<tr>
<td>6.0</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>65±6</td>
<td>2.18</td>
<td>0.22</td>
<td>0.49</td>
<td>0.38</td>
</tr>
<tr>
<td></td>
<td>0.87</td>
<td>0.104</td>
<td>0.04±0.08</td>
<td>0.043±0.007</td>
<td>0.049±0.01</td>
</tr>
<tr>
<td></td>
<td>1.23</td>
<td>0.032±0.008</td>
<td>&lt;0.04</td>
<td>&lt;0.08</td>
<td>&lt;0.05</td>
</tr>
</tbody>
</table>

^a The helium pressure was adjusted at 1.05mm instead of 1.00mm for this 3.50mm cathode for the sake of stability.

^b The helium pressure during the exposures with the 14.0 mm cathode was 0.95mm instead of 1.00mm.
Table 3

Brightness of Lines from Low Al II Levels
at Varying Cathode Temperatures and Helium Pressures
at High Current with 7.24 mm Diameter Cathode

<table>
<thead>
<tr>
<th>p mm Hg</th>
<th>100° C.</th>
<th>0° C.</th>
<th>-190° C.</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.00</td>
<td>440 ± 44</td>
<td>500 ± 50</td>
<td>350 ± 35</td>
</tr>
<tr>
<td></td>
<td>140 ± 14</td>
<td>105 ± 10</td>
<td>107 ± 10</td>
</tr>
<tr>
<td></td>
<td>12.2</td>
<td>16 ± 1</td>
<td>18.1</td>
</tr>
<tr>
<td>2.00</td>
<td>480 ± 48</td>
<td>500 ± 50</td>
<td>250 ± 25</td>
</tr>
<tr>
<td></td>
<td>110 ± 11</td>
<td>70 ± 5</td>
<td>45 ± 5</td>
</tr>
<tr>
<td></td>
<td>16 ± 1</td>
<td>19</td>
<td>11.0</td>
</tr>
<tr>
<td>4.0</td>
<td>310 ± 31</td>
<td>350 ± 35</td>
<td>150 ± 15</td>
</tr>
<tr>
<td></td>
<td>29 ± 3</td>
<td>19</td>
<td>9 ± 1</td>
</tr>
<tr>
<td></td>
<td>5.8 ± 0.6</td>
<td>6.4</td>
<td>2.3</td>
</tr>
<tr>
<td>6.0</td>
<td>270 ± 27</td>
<td>230 ± 23</td>
<td>50 ± 10</td>
</tr>
<tr>
<td></td>
<td>11.9</td>
<td>8.5</td>
<td>2.0</td>
</tr>
<tr>
<td></td>
<td>3.5 ± 3</td>
<td>3.5 ± 4</td>
<td>0.67</td>
</tr>
</tbody>
</table>

*The column of brightness at cathode temperature 0° C. is a duplicate of the column at cathode diameter 7.24 mm in Table 1.*
Table 4

<table>
<thead>
<tr>
<th>p mm Hg</th>
<th>Cathode Temperatures</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>100° C.</td>
</tr>
<tr>
<td>1.00</td>
<td>84 ± 8</td>
</tr>
<tr>
<td></td>
<td>46</td>
</tr>
<tr>
<td></td>
<td>2.6</td>
</tr>
<tr>
<td>2.00</td>
<td>110 ± 11</td>
</tr>
<tr>
<td></td>
<td>42</td>
</tr>
<tr>
<td></td>
<td>3.1</td>
</tr>
<tr>
<td>4.0</td>
<td>55 ± 5</td>
</tr>
<tr>
<td></td>
<td>7.3</td>
</tr>
<tr>
<td></td>
<td>1.6</td>
</tr>
<tr>
<td>6.0</td>
<td>2.32</td>
</tr>
<tr>
<td></td>
<td>0.064 ± .008</td>
</tr>
<tr>
<td></td>
<td>0.034 ± .008</td>
</tr>
</tbody>
</table>

a The column of brightnesses at cathode temperatures 0° C. is a duplicate of the column at cathode diameter 7.24 mm in Table 2.
Table 5

Values of Discharge Current for "Low Current" Data in milliamperes

<table>
<thead>
<tr>
<th>P</th>
<th>Cathode Diameters ((T_{\text{Cath}} = 0^\circ\text{C.}))</th>
<th>3.50mm</th>
<th>7.24mm</th>
<th>10.5mm</th>
<th>14.0mm</th>
<th>17.7mm</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.00</td>
<td></td>
<td>165</td>
<td>200</td>
<td>215</td>
<td>215</td>
<td>125</td>
</tr>
<tr>
<td>2.00</td>
<td></td>
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<th>0°C.</th>
<th>-190°C.</th>
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<tr>
<td>6.0</td>
<td></td>
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<td>160</td>
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</table>

* Discharge currents for all "High Current" data were 650 ma in all cases except for the two lowest pressures, at 0°C., with the 3.50mm cathode. At 1.05mm pressure the high current was 365 ma, and at 2.00mm it was 550 ma.
B. Precision of Measurements

Errors in the numerical values for line brightness resulted from several causes. First among these may be listed effects involving the calibration spectra. The filament temperature of the comparison lamp was readable to a precision of 5° K. This error was equal to that caused by the error of 0.02 ampere in setting the filament current.

In addition to this setting error, the accuracy of the comparison of brightness was impaired also by an uncertainty in the magnitude of the correction for aging of the lamp filament. This error was due to the lack of precise information on the relative power dissipation through radiation and conduction to the argon filling gas. The resultant uncertainty in the corrected filament temperature was about 6° K.

The total probable error in the temperature of the comparison lamp filament due to these two independent causes was thus about 7.8° K. Using Wien's approximation for thermal radiation, the logarithmic temperature derivative of the power per unit wavelength range is obtained, yielding:

\[ \frac{A\lambda}{\lambda} = 1.438 \frac{AT}{\lambda T} \], \( \lambda \) in cm, \( T \) in degrees Kelvin.

The uncertainty in the brilliance of the comparison lamp at wavelength \( \lambda \) thus varies from 2% at \( \lambda 6180 \) to 5% at \( \lambda 2490 \) Angstroms.
All of the calibration data were also affected by a random error in setting the spectrograph slit. From a statistical examination of the extrapolated characteristic curves of all plates at three sample wavelengths, the probable error in setting the spectrograph slit for the calibration exposures was 0.002 mm. This figure agrees in order of magnitude with micrometer microscope observations on the slit itself, which were made previous to the exposures. For the ultraviolet plates where the slit width used for the continuous spectra was 0.2 mm, this amounted to only 1%. However, on the visible plates, for which the slit width was only 0.03 mm, this slit setting error was 6.7%.

The other factors in the calculation of the calibration lamp brilliance, namely, the values computed from Wien's formula, the horizontal magnification and the dispersion of the spectrograph, introduced errors which were negligible in comparison to those given above.

The errors connected with the calibration source affect the absolute value of the unit of brightness in which the line brightnesses have been given. Any comparison of the brightness of measured Al II lines which were observed on different plates is thus subject to these uncertainties.

The recorded brightness values for all lines are further affected by errors in the microphotometer readings and their treatment. In the majority of cases, in which the galvanometer readings lay roughly between 3 and 40 (in which
cases the data were read from the straight-line portion of the characteristic curve), these errors did not exceed 3 or 4%. For lines stronger or weaker than these, the error of reading increased considerably. In a few cases, in which the desired lines were surrounded by above average background, the photometric errors were as large as 50%. In the graphs and tables above, the brightness values of these exceptional cases are accompanied by estimates of the photometric uncertainties.
IV. DISCUSSION

A. General Features of the Results

The brightness measurements reveal a marked dependence of the rate of Al II transitions upon the external discharge parameters. The excitation into the various quantum states of the ion is not at all what would be expected on the basis of a thermal distribution of exciting energy. This is especially true at low pressures, and with the smaller diameter cathodes. The most striking feature of the results, the peaks in the graphs of brightness versus quantum number n of the higher excited state of the series lines, is evidence of the nonuniformity of the excitation processes.

In general it may be observed that the ratios of line brightnesses for high and low currents are greater than the corresponding ratios of currents, particularly for the weaker lines. Thus the line brightnesses evidently increase more rapidly than linearly with the current, although from examination of the data some saturation effect might be suspected in cases where the excitation is very strong.

In most cases the line brightnesses increase also with cathode temperature. Here, however, the dependence is in no case very steep, and for some lines at the lowest pressure, the brightness even decreases with rising temperature.
The variations with cathode diameter and gas pressure are more complex. From the extremes of high pressures and large cathode diameters, the brightnesses of the Al II lines increase as the gas pressure or cathode diameter is reduced, until an optimum is reached near the lower extreme ranges of these two parameters. From here, however, the rates of decrease of the line brightnesses are not large.

To make possible a more quantitative understanding of even these general trends in the brightness, it is necessary to examine in more detail the actual atomic processes in the discharge. Although this examination cannot here be thorough enough to enable a complete description of the excitation, nevertheless, sufficient material may be presented for a semi-quantitative explanation of the trends noted above.

B. Interpretation of Results in Terms of Fundamental Processes

To explain the line brightnesses in this experiment, the basic problems to be solved may be phrased as follows. By what processes are the aluminum atoms introduced into the discharge, ionized and excited into the Al II states from which transitions are observed? What are the concentrations of the reacting particles in these processes, and how do they vary with the external parameters?
The discussion of these problems will involve a consideration of the major atomic processes in the discharge, and of the particles involved. These latter are accordingly listed here.

The helium gas atoms are the main constituent particles in the region, and their concentration in atoms per cm\(^3\) is represented by \(n\). The average velocity of these neutral helium atoms is \(v\). Some of these helium atoms are present in one of the metastable states, \(2^3S\), or \(2^1S\). The concentration of helium metastables is written \(n_m\), and their average velocity is also taken as \(v\). Some of the helium in the discharge region is ionized, and the concentration of these is written as \(n_+\). These ions are formed principally in the cathode region itself, and consequently have not been accelerated by any electric field; thus they may be presumed to be in rough thermal equilibrium with the neutral helium atoms. To this approximation, their average velocity is also taken as \(v\).

The atomic particles of aluminum are introduced into the discharge region as neutral atoms; they could not penetrate the dark space from the cathode wall if they were positively charged. The aluminum in the discharge region consists of both neutral atoms and ions, some aluminum having been ionized by collision with other particles within the plasma. The total concentration of aluminum is then taken as the sum of \(N_0\) and \(N_+\), where these symbolize the concentrations of
atoms and ions respectively. For the same reasons as in the case of helium, the average velocity of both the neutral and ionized aluminum particles will be taken as $V$.

The discharge contains also a cloud of free electrons. For their concentration is used the symbol $n_-$, and for their average velocity $v_e$. It must be remarked that the distribution of electrons with energy is not Maxwellian, but contains an appreciable number of rather high energy electrons. These latter are those which have been emitted from the cathode and accelerated through the cathode dark space without loss of energy by collision. Most of the concentration $n_-$ is made up of slower electrons which have been produced in collisions along with positive ions. Because of the high energy contribution to the electronic distribution, however, $v_e$ is greater than that which would be given by assuming the electrons to be distributed according to Maxwell's law, and in thermal equilibrium with the other particles. One further remark may be made about $n_-$, based on the observed fact that the region of the discharge is practically field free. This observation implies that there is no net charge in the region, and therefore the equation may be written

$$n_-=n_+ + N_+ .$$

The helium carrier gas is probably in thermal equilibrium with the walls, and the velocity distribution of its atoms
is very nearly Maxwellian. The total concentration of helium particles is then \(0.96 \times 10^{19} \frac{p}{T} \text{ atoms per cm}^3\), where \(p\) is in mm of Hg and \(T\) is in degrees Kelvin. Although the concentration of neutral excited states of the helium, except for the metastable states, will not be considered below, it may be noted that these concentrations are certainly small in comparison to \(n\).

The interactions of these particles with each other and with the walls of the hollow cathode may now be examined more closely in an attempt to calculate their concentrations. The motion of the various atoms and ions in the plasma within the cathode is described by the diffusion equation, in which the term \(\frac{\partial n}{\partial t}\) is zero in the steady state. In the case in which no sources or sinks for the particles are located inside the volume this becomes Laplace's equation, and the concentration of atomic particles is completely determined by the boundary conditions. This is the case for the total concentration of aluminum atomic particles (that is, for the sum of neutral atoms and ions). If, on the other hand, there exist processes which occur inside the volume which create or destroy the particles of interest, then additional terms must be added. For ions, for instance, these would change the steady-state diffusion equation to read

\[
D \nabla^2 n - \lambda n + R = 0.
\]
Here D is the diffusion coefficient. The term \( LN \) is the rate at which the ions are destroyed throughout the volume, and is proportional to the concentration. \( R \) is a rate at which the ions are produced throughout the volume and is taken as independent of concentration. Far from the walls, the dominance of the latter two terms give a uniform concentration \( \mathcal{N} = R/L \). The concentration in the neighborhood of the walls depends on the boundary conditions. If these are such that the wall is a sink for the particles, then the flux density at the walls is given by \( D \cdot 2\mathcal{N} \frac{\partial \mathcal{N}}{\partial x} \) where \( x \) is in a direction perpendicular to the wall. This rate of outflow may also be approximated by the effusion density \( \frac{\mathcal{N} v}{4} \), where \( v \) is the average velocity of the particles, and \( \mathcal{N} \) is then less than the average concentration in the region and may be taken as a lower limit. The rate of effusion is used as an approximation from a consideration of the diffusion process as resulting from the random motion of the particles. This is the average rate at which the particles will cross any boundary in either direction. It is only a good approximation to the extent that \( \mathcal{N'} \) is a good approximation to the average of \( \mathcal{N} \).

This provides a method for the estimation of the positive ion concentrations, for the flux density of these to the walls of the cathode is measured in the experiment as
the discharge current. If the thickness of the cathode
dark space is ignored in comparison with the radius of the
cathode, the wall current density may then be set equal to
the sum of the effusion rates of aluminum and helium ions,
giving
\[
\frac{1}{2\pi r h} = \frac{n_+ V}{4} + \frac{N_+ V}{4} \quad (1)
\]
The symbol \(i\) is here used for the total discharge current
in units of electronic charge per second, and \(r\) and \(h\) are
the radius and depth of the plasma within the cathode. The
quantities \(n_+\) and \(N_+\) may then be regarded as lower limits
on these concentrations. The presumption that the ion
concentration is approximately uniform is verified experi­
mentally by the observation that the brightness of the
discharge varies little throughout the plasma. The radia­
tion from the tube is principally from He I lines which
are excited by electron bombardment; if this is uniform
then so is the electron concentration. This then verifies
that the ions are also distributed uniformly in the plasma.

The process of cathode sputtering is an example of
diffusion in which no sources or sinks are present in the
volume. Here the total concentration inside the volume

\[\text{\textsuperscript{a}}\]

\[\text{Some of the current at the walls is carried by}
\text{electrons emitted under the bombardment of ions, the de­}
\text{excitation of metastables, and the absorption of energetic}
\text{photons. This fraction of the current, although sufficient}
\text{to supply electrons to maintain the discharge self-sustaining}
\text{is nevertheless small compared to the ion current and is}
\text{ignored above.}\]
of particles from the cathode depends on the processes at the walls alone. At the side walls of the cathode, atoms are introduced into the discharge at some rate $F_o$ dependent on the ion current densities and energies. These latter may be expected to remain roughly constant in the discharge except when the operation of the tube approached instability, as described on page 20. Bombardment of the cathode by aluminum and helium ions might be expected to involve different efficiencies of sputtering, however, and this may be represented by the use of the letters $f_{Al}$ and $f_{He}$ for the average number of aluminum atoms dislodged from the surface per ion impact for the two kinds of particles, at the energies they possess. If the fact that at least the open end of the cathode is a sink for the aluminum particles is ignored, the solution of the Laplacian results in a uniform distribution of aluminum atomic particles, and following Townes (cf. ref. 19) the rate at which they are returned to the walls per unit area may be given as the effusion density. The concentration to be used is the sum of the concentrations of ions and neutral atoms of aluminum. The rate at which atoms leave the cathode surface may then be set equal to the rate at which atoms and ions of aluminum return. This yields the equation

$$\frac{(N_+ + N_e)}{4} V = \int_{Al} \frac{n_+ V}{4} + \int_{He} \frac{N_+ V}{4}.$$  

(2)
The approximation that no sputtered atoms are lost through the open end of the cathode does not introduce serious error into the discussion so long as the ratio of length to radius of the cathode is fairly large. The average concentration of aluminum will be less than that given in the equation above if the wall area is not large compared to the open end area. Since the values of the efficiencies \( \epsilon \) are not known except in order of magnitude, however, the use of the approximation does not contribute seriously to the uncertainties in the value of the aluminum concentration. The equation may be rearranged to give the concentration of neutral aluminum atoms in the discharge region as

\[
N_0 = \frac{V}{\gamma} N_+ + (\varepsilon \alpha - 1) N_+ \quad (2a)
\]

A third equation may in principle be written describing the dynamic equilibrium which exists between the processes of conversion and re-conversion of aluminum atoms and ions. However, the processes involved here are not confined to the wall but take place throughout the volume. They are collision processes between particles representing the various constituents of the plasma. It will then be helpful to describe in some detail the general characteristics of the types of collision which are important.
Inelastic collisions among atomic particles have been divided into collisions of the first and second kinds. The former involve the conversion of part of the kinetic energy of interaction into potential energy of excitation. These are represented in the hollow cathode discharge of this experiment by the excitation and/or ionization of helium and aluminum by electron impact. The cross-sections for many of these reactions have been studied both experimentally and theoretically. In general, the energy dependence of these cross-sections is as follows: the function increases rapidly from a threshold at the excitation energy of the state, and assumes a maximum value at some energy \( E_m \). From here the cross-section falls off steadily towards higher energies. The amount by which \( E_m \) exceeds the threshold, and the shape of the curve at higher energy, depend on the type of transition involved. For instance the maxima in these curves of cross-section versus energy are much broader for ionization or for excitation through optically allowed transitions than for excitation through optically forbidden transitions. The maximum value of the ionization cross-section of an atom is in general higher than the maxima of those for excitation, but is less than that given by a billiard ball model for the collision.

Collisions of the second kind involve the transfer of potential energy of excitation from one of the interacting particles to the other. If the second particle is unable
to take up all of this energy, the remainder appears as kinetic energy of recoil: collisions in which this recoil is appreciable have accordingly been called super-elastic by some authors. A collision of the second kind may be described by the reaction equation:

$$A^* + B \rightarrow A + B^* + \delta$$

where the starred letters represent atoms in some excited state, and $\delta$ is the so-called energy discrepancy. The collision may result in exchange of charge as well as excitation: in this case for instance, $A^*$ and $B^*$ might be excited ions in the equation, and $A$ and $B$ neutral atoms. Another possibility is that the process may result in the ionization of one of the participants. In a reaction such as this, a free electron would be added on the right side of the equation, and $B^*$ would be an excited ion.

The cross-section for collisions of this type may be calculated approximately, and are discussed by Massey and Burnhop. The principal prediction is that these processes will exhibit a rather sharp resonance, the cross-sections becoming in the order of one hundred times larger than the gas kinetic values for small values of $\delta$. The resonance peaks should be sharper for the cases of simple exchange of excitation than for collisions involving charge exchange as well.
A further theoretical prediction is known as Wigner's spin rule. This states that the cross-section for such a collision will be small unless the reaction conserves the total electron spin of the system. According to Massey and Burhop, it is to be expected that this rule should be weakened if spin-orbit coupling in the atom is appreciable.

The experimental evidence concerning collisions of the second kind has been discussed in books by Mitchell and Zemansky\textsuperscript{31}, by Willey\textsuperscript{32} and others. The resonance character of the interaction has been confirmed by many investigators. Among these, Beutler and Josephy\textsuperscript{33} have performed experiments on the mercury sensitized fluorescence of sodium which are especially worthy of notice. They studied the excitation of sodium atoms from their \(3s^2S\) ground state by collision with excited mercury atoms in their \(6^3P\) states, and observed a sharp maximum of excitation of the sodium state \(7^2S\). If this excitation is presumed to have resulted from a collision of the second kind, transferring mercury atoms from the level \(6^3P_1\) to their ground state, then a positive energy discrepancy of 0.020 ev is calculated. They also found in the same experiment a much weaker maximum in the excitation of the \(5^2S\) state, which is presumably produced with the de-excitation of the metastable mercury \(6^3P_0\). The weakness of the maximum in this case is explained by the calculated energy discrepancy of 0.218 ev. The resulting collision cross-section would then be much less than in the
former case, which would outweigh the effect of the higher concentration of the mercury metastables.

The observations in support of the spin rule are not so clean-cut. Indeed, there is much experimental evidence that the rule is not very rigid. This is demonstrated in the case of helium, where the Russell-Saunders coupling is good.

Lees and Skinner\(^\text{34}\), in the course of experiments to measure the excitation of helium by electrons, observed a secondary effect which it seems possible to explain only by means of collisions of the second kind of the forbidden type:

\[
\text{He}(n^1\text{P}) + \text{He}(1^1\text{S}) \rightarrow \text{He}(1^3\text{S}) + \text{He}(n^3\text{D}) + \delta,
\]

with a very large cross-section. Massey and Burhop(ref. 30, p. 431) quote the results of further experiments by Maurer and Wolf giving the absolute values of cross-sections for collisions of the second kind which lead to exchange of excitation between helium atoms. For a collision allowed by the spin rule,

\[
\text{He}(5^1\text{P}) + \text{He}(1^1\text{S}) \rightarrow \text{He}(1^3\text{S}) + \text{He}(5^1\text{D}) + 0.003 \text{ ev}
\]

the cross-section is \(5.1 \times 10^{-14} \text{ cm}^2\), whereas for the corresponding forbidden reaction,

\[
\text{He}(5^1\text{P}) + \text{He}(1^1\text{S}) \rightarrow \text{He}(1^3\text{S}) + \text{He}(5^3\text{D}) + 0.003 \text{ ev}
\]

the cross-section is \(2.7 \times 10^{-14} \text{ cm}^2\). Thus the spin rule is not fully dependable even here.
Experiments have also been performed by Duffendack and co-workers on the "enhancement" of various lines of Pb II$^{35}$, and Cu II and Al II$^{36}$ by collisions of the second kind with neon in a special form of hot-cathode discharge tube. These results also indicate that the dependence of the excitation cross-sections upon angular momentum is not entirely in accord with the Wigner rule.

A further type of collision of importance here involves the recombination of ions in the volume of the gas. Recombination by direct collision of a positive ion and an electron, with the excess energy liberated by continuum radiation, has been studied in the atomic gases at low pressure, and also in a few cases with metallic vapors. The results of these experiments, as well as of the theory, indicates that the cross-section for such events is small. The values of the recombination coefficient for these radiative processes are of the order of $10^{-12}$ cm$^3$/sec. Although no experimental results on the recombination of aluminum positive ions and electrons are available, it seems safe to assume this value correct in order of magnitude for this case.

A second mechanism for volume recombination is the three-body collision, allowing the excess energy to be taken up as kinetic energy of a third particle. The recombination coefficient due to this process is proportional to pressure in the range of pressure of this experiment.
An attempt may now be made to apply the foregoing discussion to the problem of the relative concentrations of aluminum ions and atoms. The ionization of aluminum atoms is accomplished by two major processes. These are electronic collisions, and collisions with helium metastables. Aluminum ions may be destroyed by recombination with electrons in the plasma, or may be removed by diffusion to the walls. Each of these processes will now be considered.

Ionization by electron impact will take place at a rate given by

\[ +R_1 = N_e n_v e \sigma_e \]

Here and below, the rates \( R \) are distinguished by superscripts + or - to indicate whether the process is of production or loss, and by numerical subscripts to indicate the order of discussion. The quantity \( \sigma_e \) is an average cross-section for ionization of aluminum by electrons of these energies.

Aluminum atoms may also be ionized by collisions of the second kind with either of the helium metastables. The energy released by the helium atom in its consequent transition to the ground state is not very closely matched by any Al II state (the energy of these being measured above
the ground state of Al I). Despite this, one might expect the "resonance peak" to be broad for the reaction as it involves the detachment of an electron, so that the cross-section should be at least of the order of $10^{-16}$ cm$^2$. The rate of the reaction,

$$+R_2 = N_m v \sigma_i$$
	naturally involves the concentration of helium metastables; this may be estimated in a similar way. They are produced from unexcited helium atoms by electronic collisions, and are destroyed through collisions with fast helium atoms in which they are further excited to states from which radiative decay is possible. They are also removed from the plasma by diffusion to the walls, where they are de-excited. Both of these processes have been discussed by Mitchell and Zemansky in connection with experiments to determine the lifetimes of the metastables. Observations on the concentration of metastables in these experiments were made by an optical absorption technique after shutting off a discharge in the gas chamber. An exponential decay of this concentration was observed, for which the decay constant was found.

\[ \text{The smallest energy discrepancy in collision with a helium metastable is found in the reaction:} \]

$$\text{He I (}^2S) + \text{Al I (}^3S\text{)} \rightarrow \text{He I (}^1S\text{)} + \text{Al II (}^1D\text{)} + e^- + 0.184 \text{ ev}$$
The constant $\beta$ varied with pressure in accord with the equation

$$\beta = \frac{B}{p} + C_p$$

where $B$ and $C$ are constants characteristic of the experiment. The first term in this equation represents the rate of disappearance of metastables due to diffusion to the walls, whereas the second represents the loss through collisions with neutral rare gas atoms.

The steady state character of the diffusion processes in this experiment makes questionable the use of the first term here. The second term may certainly be used, however. For the constant $C$ in the case of helium and its metastable $2^3S$, Zemansky quotes Ebbinghaus's value of 107, if $p$ is in mm Hg.

The concentration of metastables is then obtained by equating the rates of production and loss:

$$n n_e v_e \sigma_m = \beta n_m,$$

or

$$n_m = \frac{n n_e v_e \sigma_m}{\beta}.$$

The electron velocity $v_e$ is used for the relative velocity between colliding particles. A non-committal $\beta$ is used to describe the total rate, in sec$^{-1}$, at which metastables are removed, and $\sigma_m$ represents the average cross-section for the production of helium metastables by electronic collision.
The rate of aluminum ionization by second-kind collisions may now be written

\[ R_2 = \frac{N_n n - n_e \sigma_c \sigma_m v}{\beta} \]

The conversion of aluminum ions back into neutral atoms results in part from recombination at a rate \( R_1 \),

\[ R_1 = N_+ n_- \alpha \]

Here, the symbol \( \alpha \) represents the recombination coefficient. Aluminum ions are also lost through their diffusion to the walls. In this case, in which there is reason to expect that the concentration of ions is fairly uniform, the total rate of removal of ions is equal to the current density of aluminum ions at the walls times the area over which it occurs,

\[ 2\pi rh \frac{N_+ V}{4} \]

The volume rate of loss of ions due to this cause is therefore given by

\[ R_2 = \frac{N_+ V}{2\pi} \]

Equating the total rates of increase and decrease of aluminum ion concentration,

\[ R_1 + R_2 = R_1 + R_2 \]
which yields

\[ N_n n_v e \sigma_i + \frac{N_n n_v v e \sigma_i \sigma_m}{\beta} = N_+ n_\alpha + \frac{N_+ V}{2x} \]

The concentration of aluminum ions is then

\[ N_+ = \frac{N_n n_v e (\sigma_i + \frac{nv \sigma_i \sigma_m}{\beta})}{n_\alpha + \frac{v}{2x}} \tag{3} \]

This expression might now be combined with equations (1) and (2a) to eliminate \( N_n \) and \( n_- \). The resulting expression would be rather cumbersome. Approximations may be made, however, which do not appear unreasonable on the basis of estimates of the cross-sections involved. The value of the pressure dependent part of \( \beta \) was quoted above as 107 p; with the value of \( n \) in terms of \( p \) and \( T \) calculated above this may be given in terms of \( n \) and \( T \) as

\[ \beta_p \sim nT \times 10^{-17} \text{ sec}^{-1} \]

with \( v \sim 10^5 \text{ cm/sec} \) and \( \sigma_i \) taken as \( 10^{-16} \text{ cm}^2 \), and if \( \sigma_m \) and \( \sigma_i \) are considered to be of the same order of magnitude, it is seen that the term

\[ \frac{nv \sigma_i \sigma_m}{\beta} \]

by a factor of the order of about \( 3 \times 10^3 \) at room temperature.

The decay constant of the metastables \( \beta \) contains also a term due to wall diffusion; the value of this cannot be
estimated without more information on the distribution of the metastable states. It seems safe to neglect the pressure dependence of the quantity in parentheses in the numerator at any rate, for if this additional term in $\beta$ is large, then the quotient will no longer exceed $\sigma$, by such a large margin. Equation (3) above, may then be shortened to:

$$N_+ = \frac{N_0 \nu e \nu v \sigma_i \sigma_m}{\beta (\alpha + \frac{V}{2 \tau n_{-}})} \tag{3a}$$

Using equations (2a) for $N_0$ in terms of $N_+$ and $n_+$, and equation (1) for $n_+$ in terms of $N_+$, the above may be reduced to the expression:

$$N_+ = \frac{\int \nu e \nu v \sigma_i \sigma_m \nu e}{\alpha + \frac{V}{2 \tau n_{-}} + (\nu_{+} - f_{\nu_{-}} + 1) \nu v \sigma_i \sigma_m \nu e} \tag{4}$$

If the decay constant $\beta$ has the value above, the coefficient of the combination of $f$'s in the third term in the denominator takes on a numerical value of about $10^{-10}$ cm$^3$/sec which is comparable to $\alpha$ and $\frac{V}{2 \tau n_{-}}$. If in addition the ions present are largely helium, the dependence of $n_-$ on $N_+$ may be neglected and the equation for $N_+$ assumes the form

$$N_+ = \frac{A}{2 \pi \nu T n} \cdot \int \nu e \sqrt{T} \tag{4a}$$

$$\alpha + \frac{\sigma}{T} \sqrt{T} + DT$$
where $\alpha$ is proportional to pressure and to $1/T$, and the $\sqrt{T}$ factors come from the velocities. The brightness of the various spectral lines of Al II should be roughly proportional to this concentration, and to the concentration of the particles which excite the aluminum ions into the initial states of these transitions.

If the aluminum ions are produced primarily by collisions of the second kind between ground state aluminum atoms and helium metastables, the aluminum will be left principally in the Al II $3^1D$ level as noted in the footnote on page 81. From this level they may decay radiatively to the $4^1P$ state with rather low probability (the spectral line corresponding to this transition is at 3.15 microns, in the infra red) and to the $3^1F$ state with a rather high probability and giving rise to the ultra-violet line $\lambda$1989.8 A. The relative probability of these two transitions is given by the $\nu^4$ consideration to be about $6 \times 10^4$. From the $3^1P$ state another high-probability transition is possible to the $3^1S$ ground state of Al II, even further in the ultra violet. Neither of these latter two transitions were observable in the wavelength range of the present experiment. The brightness of these lines would have served as a useful check on the ionization mechanism postulated above, and it is unfortunate that they were not accessible for measurement here. The few newly-produced ions in the $3^1D$ level which decay radiatively into the $4^1P$ state then drop further into the
4\textsuperscript{1}S state, from which originates the \( \lambda 2816 \) line, or into
the \( 3p^2 \, ^1D \), thence to go also to the \( 3^{1}P \) with the emission
of \( \lambda 3900.7 \). Thus they contribute to the intensity of two
of the lines observed from the lower Al II levels. Most of
the population of these levels probably comes from electronic excitation of the Al II ground state however, and the
brightness of the lines from them must therefore be further
dependent on the electron concentration.

Together, these considerations lead to the expectation
that the lines corresponding to these and other transitions
from states populated in this way should be proportional to
the square of the wall current density.

Similarly, the dependence on carrier gas pressure of
these lines should be of the form \( \frac{1}{A + Bp} \). Without a more
precise knowledge of the recombination coefficient it is
not possible to predict the relative magnitude of \( A \) and \( Bp \).
It may be noted however that the equation (4) does predict
that this pressure dependence should be greater for the
larger cathodes than for the small.

The form of temperature variation of the concentration
of Al II depends on the relative magnitude of the term in
the denominator of equation (4a), and on the possible tempera-
ture variation of the values of the sputtering efficiencies
\( f \).

The brightnesses of lines of Al II which represent tran-
sitions from highly excited states of the ions are further
dependent on yet another type of excitation process. Such a process may involve collisions of the second kind between low-lying Al II levels and excited states of He I. For such collisions to be very frequent, their cross-sections must be rather large, for certainly the concentrations of most excited states of both Al II and He I are not large.

A search of the tabulation of energy levels of Al II and of He I has revealed a few dozen such possible collision reactions. Some of the higher series members of Al II, from which transitions were observed, were capable of excitation by three or four different collisions which involved low values of energy discrepancy. For instance, the 81F level of Al II could be excited by the following transitions:

\[
\text{He}(5^3P) + \text{Al II}(5^3S) \rightarrow \text{He}(2^3P) + \text{Al II}(8^1F) + .0027 \text{ ev}
\]
\[
\text{He}(3^3S) + \text{Al II}(5^1S) \rightarrow \text{He}(2^3S) + \text{Al II}(8^1F) - .0044 \text{ ev}
\]

The line \( \lambda 2881.5 \) originating on the 81F level of Al II was observed to have much larger intensity than its series neighbors at low pressures.

Similarly the 93G levels might be populated by the reactions:

\[
\text{He}(4^3P) + \text{Al II}(4^3D) \rightarrow \text{He}(2^1S) + \text{Al II}(9^3G) + .00073 \text{ ev}
\]
\[
\text{He}(3^1P) + \text{Al II}(5^3S) \rightarrow \text{He}(2^3S) + \text{Al II}(9^3G) + .0035 \text{ ev}
\]
\[
\text{He}(3^1S) + \text{Al II}(5^1S) \rightarrow \text{He}(2^3S) + \text{Al II}(9^3G) - .0050 \text{ ev}
\]
\[
\text{He}(3^1S) + \text{Al II}(4^3D) \rightarrow \text{He}(2^3S) + \text{Al II}(9^3G) + .0093 \text{ ev}
\]

The line \( \lambda 4347 \) from the level 93G was also brighter than its series neighbors at low pressures, in the smaller
cathodes.

On the other hand, several possible collision reactions with low energy discrepancy and presumably large cross-sections may be found for the excitation of the Al II levels 10^3 G:

\[
\text{He}(5^1S) + \text{Al II}(5^3S) \rightarrow \text{He}(2^1S) + \text{Al II}(10^3G) + .0031 \text{ ev}
\]

\[
\text{He}(4^3S) + \text{Al II}(4^1F) \rightarrow \text{He}(2^1S) + \text{Al II}(10^3G) + .0047 \text{ ev}
\]

\[
\text{He}(4^3S) + \text{Al II}(4^3F) \rightarrow \text{He}(2^1S) + \text{Al II}(10^3G) - .0017 \text{ ev}
\]

The line λ4160, from this 10^3 G level was in every case weaker than its series neighbors.

If these and similar processes are to be considered as an explanation for the observed peaks in the intensities of lines from the higher series members, a quite non-uniform population of the lower excited states of Al II or He I must be postulated. Such non-uniformities in the distributions of excited states might be expected to arise in both cases due to the presence of metastable states in the energy level schemes of the atomic system. In He I, the 2^3S and 2^1S levels are metastable, and in Al II, the 3p \(^{3}P_{0}\) and 3p \(^{3}P_{2}\) states are metastable. These might well lead to an over population, not only of these states, but also to states immediately above them which could be repeatedly excited by the process of imprisonment of their resonance radiation to the metastables. The concentration of metastable aluminum ions would be proportional in this range to the reciprocal of the helium gas pressure, for they would be liable to
collisions which would shift them to the $3^3F$ state, from which radiation is possible. The only line from this state is the intercombination line $\lambda 2669$ however, and so the lifetime of this state $3^3F$ would be expected to be large.

Despite the plausibility of these processes, much more complete analysis of the brightnesses of these and many more lines of the Al II spectrum would be needed before this model could be believed. It is suggested merely that this might be a possible mechanism for the production of the observed peaks.
V. SUMMARY

The experimental part of this research involved measurements of the brightness of a hollow cathode discharge in the light of various wavelengths of the first spark spectrum of aluminum. The hollow cathode tube was constructed in accord with modern specifications for a light source for high resolution spectroscopy. The line brightnesses were measured under various conditions of operation of the discharge tube. The external parameters which were varied were discharge current, cathode temperature, carrier gas pressure and cathode diameter.

The motivation for the experiment was two-fold. Firstly it was desired to obtain empirical information on the optimum conditions for the operation of this type of source for the production of spectra, and, secondly, data were sought which might help to clarify the atomic excitation processes. Both of these objectives have been attained to some extent.

In general it has been found that the brightness of the source is roughly proportional to the square of the wall current density. There is an optimum pressure for operation of the discharge which is dependent on the cathode diameter and, to some extent, on the cathode temperature and on the particular atomic lines to be excited.
The average line brightness at constant current varied approximately inversely with the square of the cathode diameter. From the quadratic dependence of brightness on wall current density noted above, this implies that cathode diameter has little or no effect on the brilliance of the source. The total light output from the discharge should then vary directly with the square of the cathode diameter, a result which is not inconsistent with the observations of Winger\textsuperscript{37} of the spectrum of Pb II in a hot hollow cathode.

It has been found possible to explain in a rough way the features of the brightness variations by making a number of approximations concerning the physical processes within the discharge, and some rather crude estimates of the magnitudes of various important but unknown constants of the atomic interactions. In addition a mechanism has been proposed for the preferential excitation of certain excited states of the aluminum ion, which lead to the peaks observed in the brightnesses of several series of atomic lines in its spectrum.

In addition the observations of Sawyer\textsuperscript{38} on the "limit of excitation" of the Al II spectrum in the type of source have been confirmed.
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