VARIATION OF HELIUM INTENSITITES WITH CURRENT DENSITY AND PRESSURE.

T H E S I S

- By Walter C. Michels -

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1 9 3 0

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A B S T R A C T

A review of the literature on the subject of the excitation function of helium shows wide discreptancies in the experimental results. The author has attempted to trace the sources of these differences and has found that there are two aspects in which the experimental conditions differ from ideal. These are:

1. A failure in the production of a homogenous electron beam.
2. Deviations of the excitation conditions from simple excitation.

The first of these difficulties has been overcome, to a very large extent, by the use of a specially designed discharge tube. The development of this tube, together with the improvements in the homogeneity of the electron beam, is traced.

In respect to the second point, it is shown that the criterion for simple excitation is a linear dependence of intensity on current or pressure. This has not been obtained, in general, by previous workers. With the apparatus mentioned above this linear relationship is obtained only by proper cleaning of the tube. The final results show linearity within the experimental error.

The intensities have been measured by a new modification of the Ornstein-Dorgelo method.

VARIATION OF HELIUM INTENSITIES WITH CURRENT DENSITY AND PRESSURE.

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1. Introduction. The problem of the variation of intensity of line spectra as the conditions of excitation are changed is one which has claimed considerable interest for a number of years, both from the experimental and theoretical standpoint. Certain special cases, particularly the relative intensities of multiplets, have been treated in a very successful manner from both angles, while the more general problem of the changes of intensity of any line has not been so happily consummated. I believe that no successful theoretical attempt to derive the excitation function (i.e. the dependence of intensity on the velocity of the exciting electrons) has been made, although Dr. Oppenheimer tells me that the general nature of this function can be understood in a qualitative way.

Experimentally the problem is in very little better condition than theoretically. A number of investigators, it is true, have measured the variation of intensity as the voltage of the electrons has been changed, but the disagreement between results may be classed as one of the most striking considerations in comparing the various papers.

A very large part of the measurements have been made on helium for two reasons:

1) The simplicity of the spectrum, the high excitation voltage and the ease of purification make it an ideal substance for spectroscopic work.

2) From the theoretical viewpoint, the relative simplicity of the atom and the relations of the singlet and triplet systems make helium of some interest.

In the first work on the subject, Hughes and Lowe[1], using the neutral wedge method of Merton[2] investigated the variation of intensity of about eight lines of the spectrum when the electron accelerating potentials were varied from 34 to 210 volts. Their results give, for all lines of the triplet system a constantly decreasing intensity with increasing voltage, and for the singlet system, a relatively flat maximum of intensity at voltages of between 60 and 210 volts. If the triplets show a maximum, this work would indicate it to be below 34 volts.

At about the same time, Udden and Jacobsen[3] made a very qualitative study of the excitation function and showed that, between 27 and 90 volts, the singlet system gained in relative intensity over the triplet system as the velocity of the impinging electrons increased. This furnished a qualitative check on the results of Hughes and Lowe, but contributed nothing new to the field. Bazzoni and Lay[4], however, attempted a quantitative determination and obtained curves on which the intensity, in general, increased rapidly with increasing potential from 24 to 90 volts for the singlets and approached a maximum for the triplets at about 50 volts. Even for these lines, however, there was very little decrease in intensity between the maximum and 90 volts.

For a few years after the conclusion of this work, little was done on the subject. About 1927, interest was reawakened by the development of Professor Orstein's method for measuring intensities by the "shift of density" curves. The following year, Orstein, Burger and Kapuscinski[5] and Hodges and the author[6] investigated the dependence of intensity on pressure in the Geissler discharge. The results seemed impossible of any theoretical interpretation, indicating only that the singlet system was favored relative to the triplet as the pressure decreased, and that the

higher members of the series were likewise favored relative to the lower. Maxima of intensity for all lines were observed at pressures of 3-4 mm. It may be noticed that, if we assume that the changes of intensity are due to the variations of electron velocity which occur with the lengthening of the mean free path as the pressure decreases, the relative behavior of the singlets and triplets would agree in a qualitative way with the results of Hughes and Lowe.

At about the same time, Cornog[7], using apparatus almost identical with that of Bazzoni and Lay, studied the excitation function of a few lines of helium for 50 to 60 volt electrons and found sharp maxima for these lines at 54.2 volts.

The first work on the excitation functions with the new methods of intensity measurements was made at Utrecht by Peteri and Elenbaas[8], who found intensities continuously increasing with voltage from 30 to 60 volts. Closely following this Hanle[9] published what is probably the best work done on the excitation function to date. After an attempt to eliminate errors due to space charge, secondary electron emission, etc., he obtained curves of intensity vs. voltage which agree in a qualitative manner with those of Hughes and Lowe. The triplets show maxima at about 30 volts, while the singlets have much flatter maxima at 50 to 100 volts, at considerably lower energies than in the earlier work.

After modifying the apparatus used in his earlier work, Elengaas published a second article[10]. His results give two maxima for most of the lines, one occurring at 30-40 volts, the other varying from 60 to 150 volts, depending on the line.

The results to date then, may be summed up:

1) The triplets probably show a maximum intensity slightly above the ionization potential.

2) Higher voltages favor the singlets over the triplets.

3) Among seven papers published on the subject of the excitation function, no two give a quantitative agreement, to anything like the precision obtainable in the intensity measurements themselves.

2. Scope of the Work. It has seemed to the author that the principle problem in the study of the excitation function has been to find and remove the sources of error which have caused these wide discrepancies in the published data. In order to see in what direction search is most probable, it may be well to define the excitation function somewhat exactly. For convenience in theoretical considerations, it seems that the best definition would be "the probability that a light quant of the particular wave-length considered be emitted when an isolated atom experiences an impact (defined, for example, by kinetic theory considerations) with an electron moving with a velocity v."

If we take such a definition two questions in regard to the experimental conditions obtained in the various researches arise:

1) Was the velocity of all electrons causing excitation known?

2) Did the emitting atoms act truly as "isolated" or were such perturbing affects introduced by the apparatus and neighboring atoms and electrons that the results are meaningless from the theoretical viewpoint?

In attempting an answer to the first question, we may consider some of the ways in which the electron stream might be made inhomogenous. A casual inspection shows five possible sources of extraneous electron currents:

1) Secondary emission from the electrodes.

2) Reflection of electrons from the electrodes.

3) Free electrons resulting from ionization.

4) Photoionization due to emission, particularly of the line at 585 A.

5) Photoionization due to X-rays from the electrodes.

Of these five, the first two are the ones which take place with the highest efficiency, and are likely to be most serious. In reviewing the papers, it appears that Hanle is the only worker in the field who constructed his discharge tube in such a manner as to prevent these secondary electrons from being emitted in large quantity at the plate. But neither he nor any other author gives any indication that he has determined the velocity distribution of his electron stream. Moreover, as will be shown later, in apparatus essentially equivalent to that used by all workers, a retarding potential test shows that the distribution of electron velocities is far from uniform.

The second question is somewhat more fully answered in the published reports, as we know what to expect from a theoretical viewpoint if the atoms behave independently of each other. Both theory and experiment show quite definitely that the number of transitions occurring in a gas is proportional to the number of atoms in the initial quantum state. But if each atom acts independently, it is clear that this number will be proportional to the number of impacts occurring. Combining the constants of proportionality into k we have:

$$I = k\,n$$

where I is the intensity of the emitted radiation and n is the number of electron impacts per unit time. Now from kinetic theory, the number of collisions occurring in a distance a if N electrons start out is

$$n = N\left(1 - e^{-\frac{a}{l}}\right)$$

where l is the electronic mean free path. Since l is inversely proportional to the pressure p, and since in all the work, the pressure is kept sufficiently low so that the electron mean free path is long compared with the dimensions of the apparatus, we may substitute b/p for l and expand the exponential. If at the same time, we use the fact that the number of electrons is proportional to the current i

$$n = c\, i\, p$$

$$\text{or} \quad I = k_1 i\, p$$

That is, the intensity should vary linearly with the current and pressure in the range used if the atoms act in an isolated manner.

Most of the workers have made some sort of a test of this point. Hughes and Lowe reduced their pressure by a factor of 2.75 and made one run. The observed changes of intensity varied by factors of from 3.2 for 3889 A. to more than 8.9 for 3965 A. They also reduced their current to 1/2.90 of the original value and obtained intensity variations from 2.3 to 5.1 times. Hanle states that the linearity of the 3889 A. with current was fairly good, and states, without quantitative data, that the pressure dependence was not as great as that found by Hughes and Lowe. The best test of current dependence was probably made by Elenbaas who varied the current density by a factor of 100 and found a 300-fold variation of intensity. He also worked at two pressures, 0.04 mm Hg and 0.10 mm Hg, and found marked differences in the results, particularly in the relative intensities of the various lines.

From a study of these results, it has seemed clear to the author that the inconsistencies of the present data are probably due to a failure of the experimental conditions to approach the ideal state of independence of the emitting atoms. This thesis will deal with an attempt to

show that this ideal state can be achieved within the present limits of accuracy of good intensity measurements.

3. Measurement of Intensities. In the earlier part of the work, the photographs were taken with an 83 cm concave grating, using the shift of density method developed by Orstein and Dorgelo[11] and modified by Hodges and the author for direct comparison against a standardized lamp[6]. This arrangement soon showed itself unsuitable, due to the fact that it necessitated exposures of two or three hours, during which it was very difficult to maintain conditions steady with sufficient nicety.

Consequently a glass spectrograph with an F 2.7 telescope lens was used in the latter part of the work. As the collimator had a focal length over six times as great as that of the telescope, the image of the slit at the plate was only about 3 mm in length, and the stepped reducers used in the Orstein method could not be applied. A further difficulty presented itself due to the necessity of supplying a continuous comparison source of the same order of intensity as the line spectra.

These troubles were removed by the use of the optical system shown in Fig. 1 and by a new method of plate calibration. The F 4.0 condensing lens was used to focus the image of the discharge on the slit, while a beam from the standardized tungsten lamp was carried in from the side and allowed to fall on a small right angles prism mounted on the optical axis. The front face of this prism was ground to a focal length of 25 mm, so that an image was formed just ahead of the lens. This image could then be used as a secondary source, and only the light intercepted by the slit, half a meter away, was used for calibration of the plates.

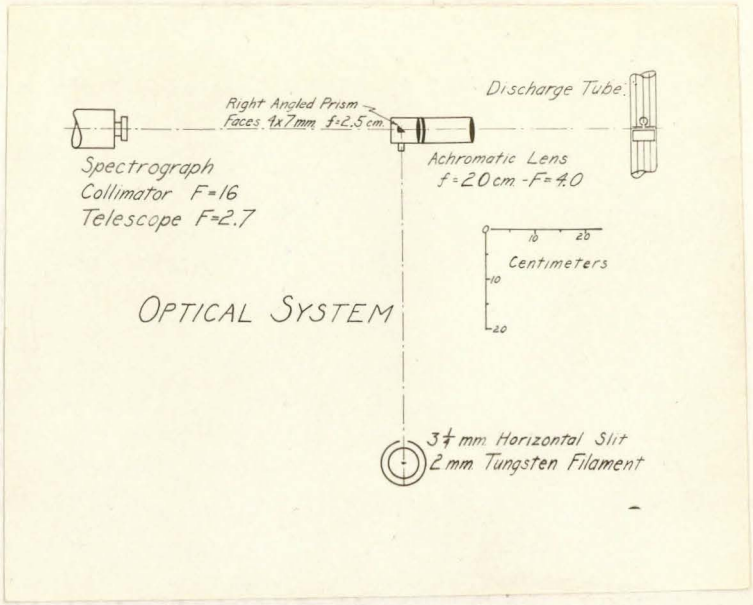


FIG. I- OPTICAL SYSTEM

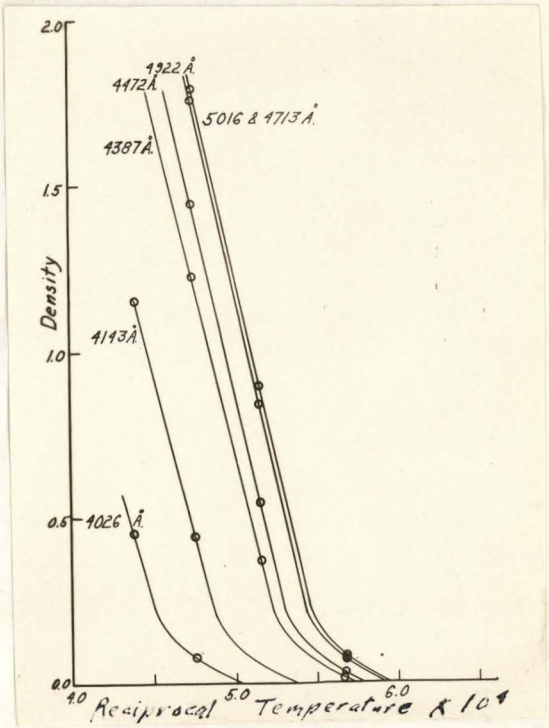


FIG. II- CALIBRATION CURVES

Besides reducing the intensity in about the required ratio, this arrangement has the advantage that it enables successive exposures to be made without moving any of the apparatus. This, in turn, made it possible to secure exposures with known intensity ratios by taking several exposures, all with the same time, and with the temperature of the standard lamp as a variable. In the older method, the density is plotted against the logarithm of the intensity. This plot has the advantage that, over a large range of exposures, it gives very nearly a straight line, since the plate obeys the Swartzchild formular

$$D = \gamma \log (I t^{p}) = \gamma \log I + c$$

if the exposure time is constant. It would be possible, of course, to calculate log I as a function of temperature for all the wave-lengths used, and to plot the curves in this way.

Such a procedure, however, would be rather laborious, and a much simpler method is available. In the range of wave-lengths used, it has been shown[12] that tungsten follows very closely Wien's law:

$$I_{\lambda,T} = \epsilon_{\lambda} c_1 \lambda^{-5} e^{-\frac{c_2}{\lambda T}}$$

where c_1 and c_2 are known constants, λ the wave-length and T the temperature in degrees Kelvin, while the emissivity, ϵ, is a function of λ and T. The dependence of the last on temperature, however, is small, and if we consider ϵ to be constant, then as we vary the temperature for a given wave-length, we find that

$$I_T = a\, e^{\frac{-b}{T}} \quad (a \text{ and } b \text{ are constants})$$

or

$$\log I_T \propto -1/T$$

Consequently, if the density is plotted as a function of the reciprocal temperature the same straight line results as in the previous method. A

typical calibration cruve obtained by this method is shown in fig. 2.

The calibration thus obtained gives a relation between density produced on the plate and temperature of the tungsten filament. If the density produced by the line being measured is then taken, the temperature at which the lamp would have to be run to produce the same intensity with the same exposure time can be found. Using Worthing and Forsythe's data[12] in conjunction with Wien's law, one can calculate the energy distribution of the lamp, and consequently, the intensity of the line in question.

In the above discussion, it has been assumed that other physical and chemical factors, such as those determined by development conditions, are kept constant. To insure this, each plate was calibrated separately, and the development was carried out following the "brush development" procedure of Bloch.[13] The plates were soaked in running water for five minutes before development, then were brushed continuously with a soft camel's hair brush during the three and one half minutes of development in a mixture of one part of Eastman D-61 a elon-hydroquinine developer with two parts of water.

With this procedure, repeated runs with conditions as nearly identical as possible differed among themselves by 5 to 10 percent, in general. The occasional large fluctuations of 20-50 percent which may probably be attributed to variations in the emulsion over very small areas of the photographic plate were not eliminated, but occurred so seldom that checks left no doubt that they were spurious.

4. Design of the Discharge Tube. It was hoped, at the start of thiswork, that it might be possible to use the very simple discharge tube shown in fig. 3. A very short period of trial, however, convinced me that the design possessed several serious disadvantages:

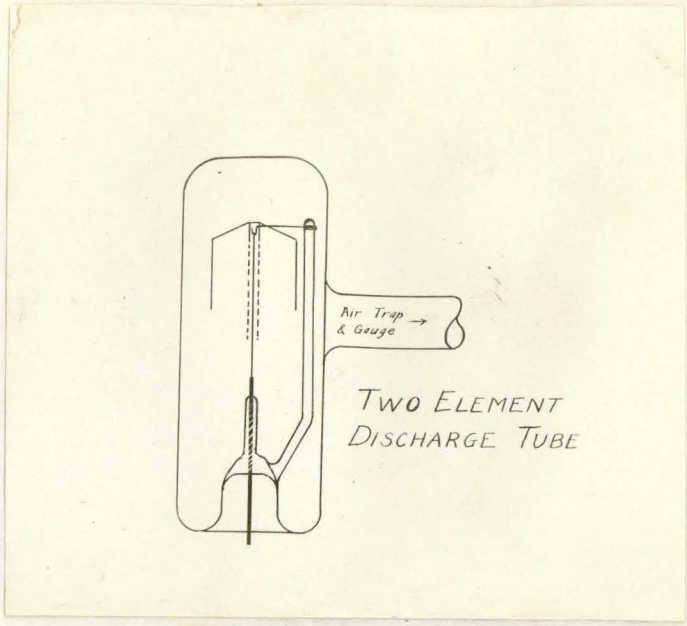


FIG. 3- TWO ELEMENT TUBE

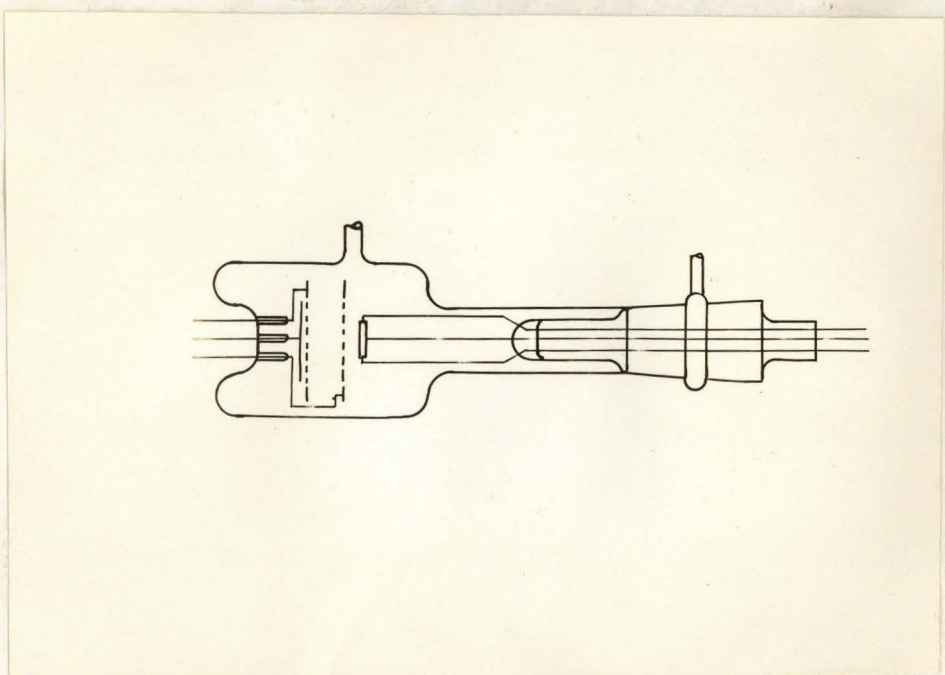


FIG. 4- UNIPOTENTIAL CATHODE TUBE

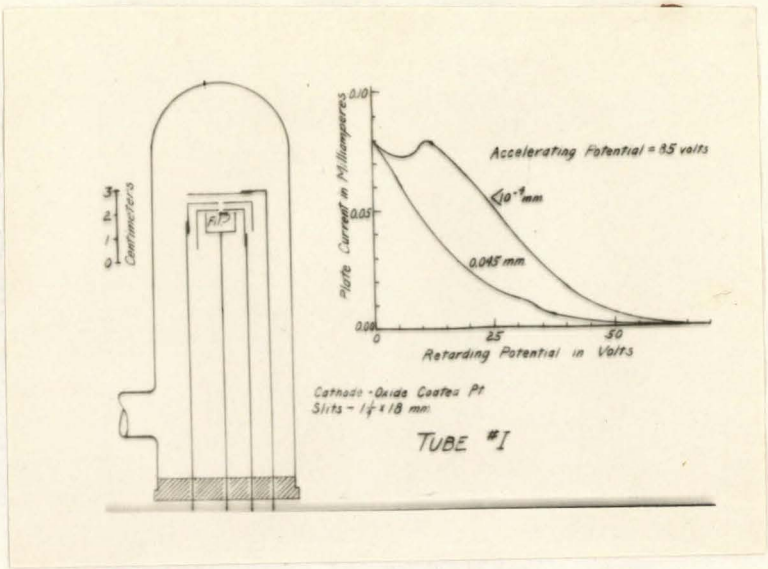

Centimeters
Plate Current in Milliamperes
Accelerating Potential = 8.5 volts
<10⁻³ mm
0.045 mm
Retarding Potential in Volts
Cathode - Oxide Coated Pt
Slits - 1/4 x 18 mm
TUBE #I

FIG. V

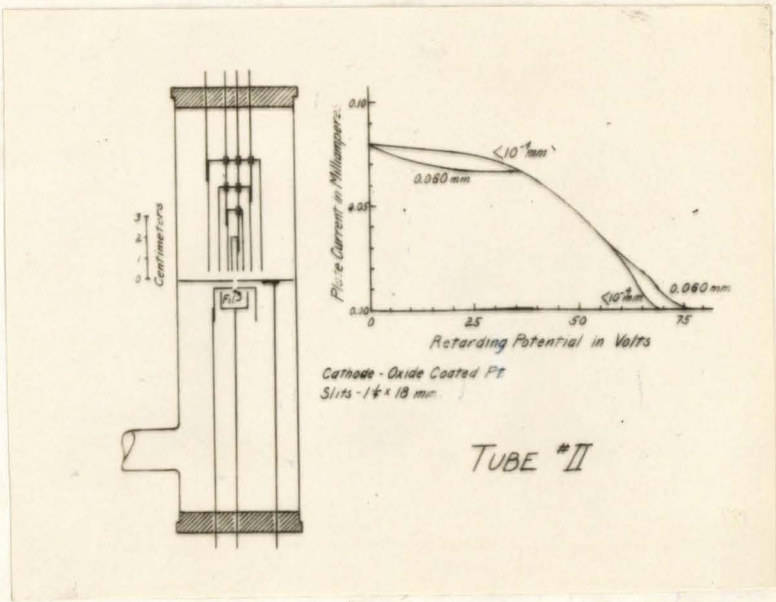
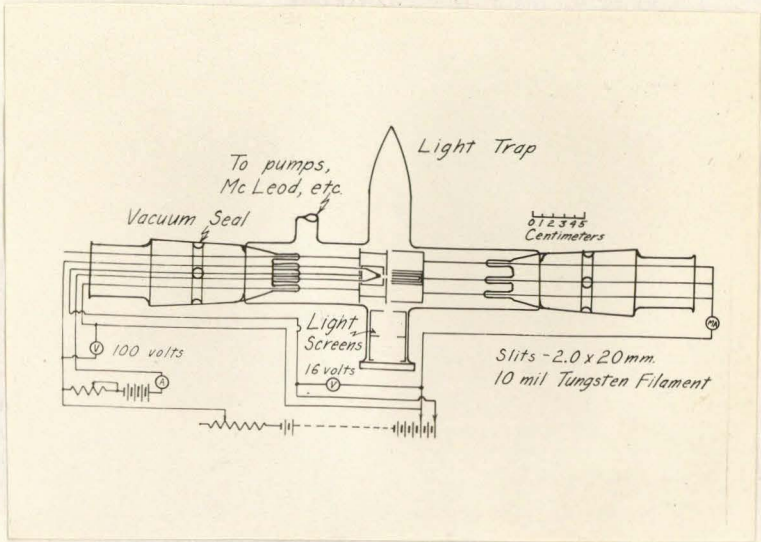

Centimeters
Plate Current in Milliamperes
<10⁻³ mm
0.060 mm
<10⁻⁴ mm
0.060 mm
Retarding Potential in Volts
Cathode - Oxide Coated Pt
Slits - 1/4 x 18 mm
TUBE #II

FIG. VI

1. The potential drop across the long tungsten filament caused an appreciable spread in the electron velocities.
2. No means of determining the velocity distribution of the electrons was provided.
3. Conditions of operation when helium was admitted to the tube were so unsteady that it was evident that an arc must be taking place.
4. The continuous background of the filament was large compared with the density produced by the lines themselves.

In an attempt to overcome these difficulties a second tube was designed, and is shown in Fig. 4. A second grid was inserted to enable retarding potential tests of the velocity distribution, and a unipotential cathode was used. The velocity tests showed a fairly good electron distribution in vacuo, but a great spread of velocities when the helium pressure was at all workable. The steadiness of the discharge was not appreciably improved over the previous tube.

After some work with this design, it became apparent that the difficulty arose from the fact that the dimensions of the tube were large compared with the mean free paths of the atoms. This enabled positive ions to be accelerated in the field and to cause secondary ionization, as in an arc. A rather radical departure from previous designs was therefore made and the tube shown in Fig. 5 was put into use. Tests of the dependence of intensity on current and pressure were immediately made, and instead of the linear law expected, it was found that the variation was with a power greater than one for the pressure and less than one for the current. This suggested that the true current was not that measured by a meter in series with the plate. If a large number of secondaries with speeds sufficient to excite the atoms were present, exactly such an affect would be expected. The presence of such secondaries is confirmed by the evidence of the retarding potential curve in



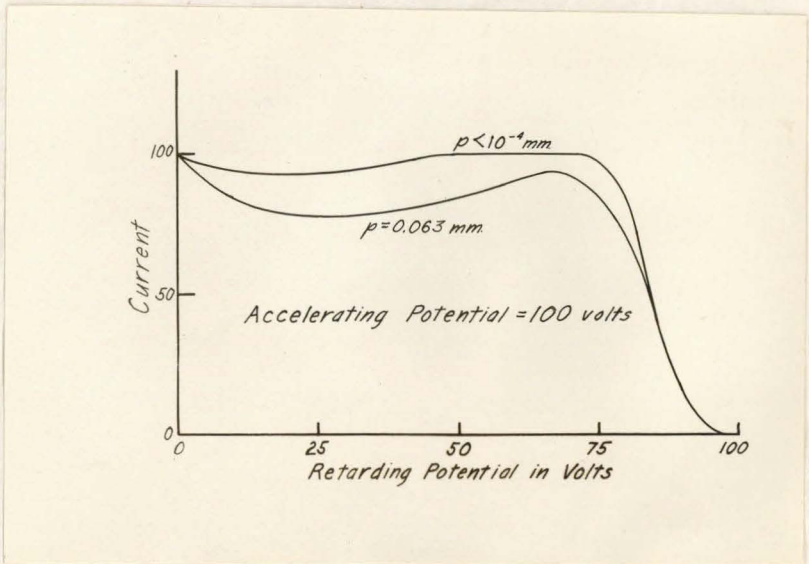


FIG. VII- FINAL DESIGN OF TUBE
with
ELECTRICAL CONNECTIONS AND
VELOCITY DISTRIBUTION CURVE

Fig.5, which shows that there is not even a predominant velocity when a constant accelerating potential is applied, either in vacuo or this gas.

One might expect the greater part of the secondary emission to come from the plate, and consequently the design shown in Fig. 6 was next tried. In this tube, the plate was so constructed as to approximate a perfect cavity for the electrons. Most of the secondaries emitted from the plate would be expected to hit the large exposed surface rather than atoms of gas in the space observed spectroscopically. As may be seen from the retarding potential curves, a great gain was made by this construction, but the velocity distribution was still far from ideal, even in vacuo.

Up to this point, oxide coated filaments had been used in all the designs, because of the low temperature at which they could be run. This had the double advantage of cutting down the continuous light from the filament and of enabling a smaller difference of accelerating potentials for electrons from the two ends of the emitting surface. It was suggested by Dr. Mackeown, however, that the low work function of the barium used in these cathodes, combined with the high vapor pressure, might be a liability rather than an asset, due to the fact that the material might distill to the slits of the electrodes and there act as a very efficient source of secondary electrons. It seemed worth while, therefore, to try a similar design of tube with a tungsten filament. Several trials were made in this direction, and the apparatus finally evolved is shown in Fig. 7. The arrangement of the electrodes is not essentially different from that of the previous type. The light from the filament, however, was a serious difficulty, and it was necessary to introduce the light trap and the screens as shown, in order to reduce this to a small fraction of the line intensity. The tube, as shown, was used in all the final measurements.

The velocity distribution curves shown in the ~~first~~ figure give an idea of the improvement accomplished by the use of tungsten. It is of interest to note that in nearly all recent work on the excitation function, oxide coated cathodes have been used, in designs quite similar to these tubes, and it is therefore highly probably that the electron streams were not more homogenous than would be indicated by Fig. 6.

5. Variation of Intensity with Current Density and Pressure.

In section II, it was shown that if simple excitation and emission are taking place at low currents and pressures, that a linear relation would be expected between intensity and pressure or intensity and current. An attempt will now be made to estimate how closely this condition of simple excitation is satisfied in the apparatus used for this work.

The highest pressure ever used for exposureswas 0.10 millimeters of mercury, and the highest current was one milliampere. As the area of the slits was 80 sq. mm., this gives a current density of 0.0125 amperes/sq. cm., or about 10^{17} electrons per sq. cm per sec. If this current be considered to be passing through a centimeter cube of the gas, the number of collisions made will be

$$(1 - e^{-1/\ell}) \, 10^{17}$$

where ℓ is the mean free path of the electrons, given as 1.02 cm at 0.10 mm pressure, by kinetic theory. Calculating this we find that there will be $6.2\ (10)^{16}$ collisions per second. But the number of atoms in the cube is $0.55\ (10)^{16}$, so each atom will experience a collision on the order of once each tenth second.

Two processes other than simple excitation may be considered as possibilities. One is due to the existence of metastable atoms, which may either collide with each other, producing one ionized and one neutral atom or be struck by an electron before returning to the normal state. The life-time of these states, however, has never been determined to be greater than

10^{-1} seconds and hence, even at the highest current and pressure (which were never used simultaneously), the chance of an electron striking an atom in the excited state is small. The mean free path of an atom, moreover, at 0.10 mm is about two millimeters, and the mean distance which from any point in the space where excitation is taking place to an electrode surface is less than this, so the chance of collisions between metastable atoms before they reach the wall is negligibly small.

The second process is one of ionization and recombination. If we assume that any positive ion on striking an electrode is neutralized, the chance of this type of emission is negligible. For the velocity of thermal agitation is of the order of 10^5 cm per second and consequently the time required for a positive ion to reach the electrode is around $5\ (10)^{-6}$ seconds. Even if each collision results in an ion, the concentration of positives will remain very small, as they will diffuse out much faster than they are formed. In addition, any concentration of positives would result in a space charge which would repel the positives very rapidly. If a space charge is built up so that the potential at the center of the space is one volt above that of the electrodes, the positive ions will be given a velocity of about $4\ (10)^6$ in one mean free path. This, added to the thermal velocities would certainly result in a low concentration of positive.

From these considerations, it would seem highly probably that the apparatus should approximate very closely the ideal conditions hoped for, In the first work done with this tube this, however, was not the case, for the intensities, when plotted against either current or pressure gave a variation decidedly not linear. The relation for any given line could be expressed approximately by the formula:

$$I = k_1 ip \not / k_2\ i^2 p^2$$

where, with 100 volt electrons, k_1 and k_2 were of the same order of magnitude. With decreasing voltage, k_2 decreased until it became negligible at about 60 volts.

Repeated runs shows that, while k_1 remained constant, k_2 varied from run to run. A search for the cause of this variation eventually indicated that the latter constant could be brought to zero by sufficient cleaning of the electrodes by electron bombardment. The following procedure was therefore adopted:

1. A charcoal trap, adjoining the tube, was baked at 350°C for twelve to twenty-four hours, until the pressure in the system was less than 10^{-4} mm of mercury.
2. With the charcoal still heated, the filament was started and the emission gradually built up to two or three milliamperes with an accelerating potential of 250-300 volts. Immediately before the exposures were taken the tube was run, in a good vacuum, and with the charcoal trap at liquid-air temperature, with the above current and voltage, for five or six hours.

The results of a series of these exposures are shown in Figs. 8-15. The pressure was varied from 0.007 to 0.096 mm, and the current from 0.050 to 1.00 milliamperes, the accelerating potential being held constant at 100 volts throughout the work. As the dependence of both current and pressure was linear, space has been saved by plotting the intensity in arbitrary units against the product of current in milliamperes and pressure in millimeters. All observed points have been plotted, and while the occasional large variations noted above take place, it is apparent that within the accuracy of the intensity measurements, there are no systematic deviations from linearity.

The reason for this change in the behavior of the intensities is somewhat doubtful. The only reasonable explanation seems to be that the assumption that the ions are neutralized on collision with the electrodes may be invalid when a film of atmospheric gas or stopcock grease vapor

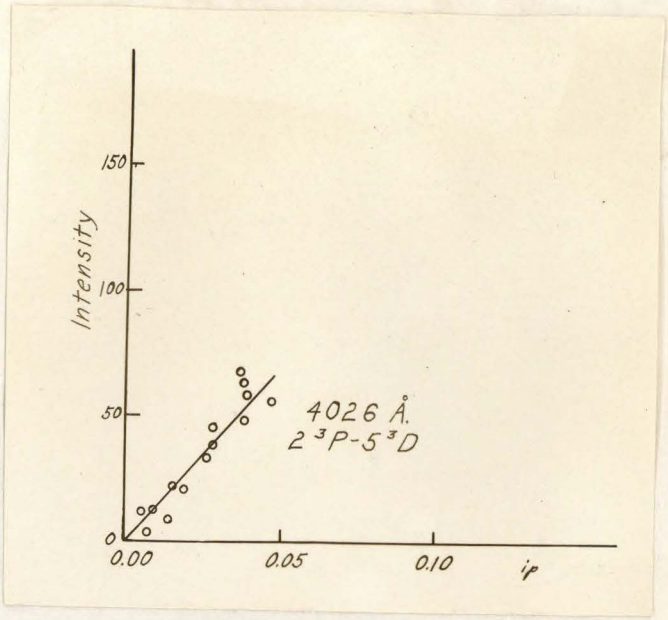


FIG. VIII

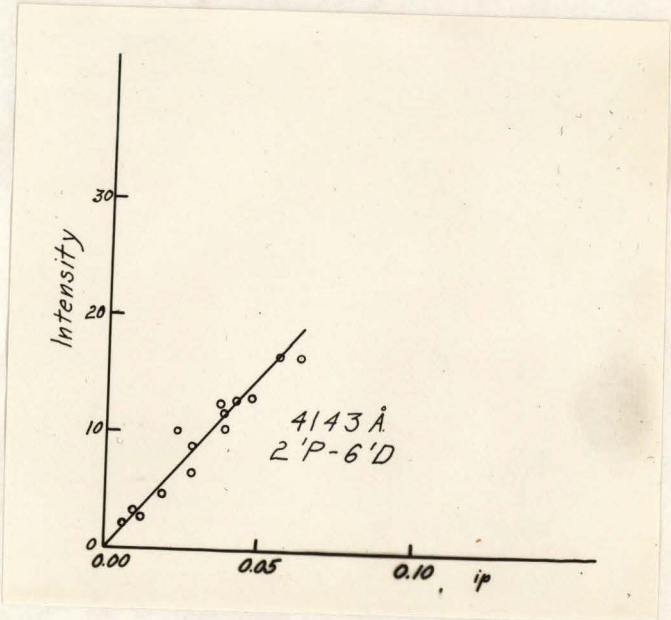


FIG. IX

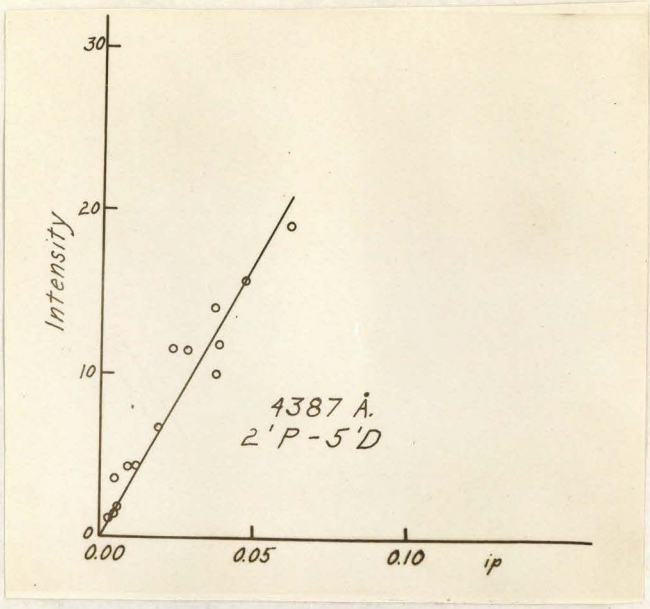

30
20
10
0
Intensity
4387 Å.
2 'P - 5 'D
0.00
0.05
0.10
ip

FIG. X

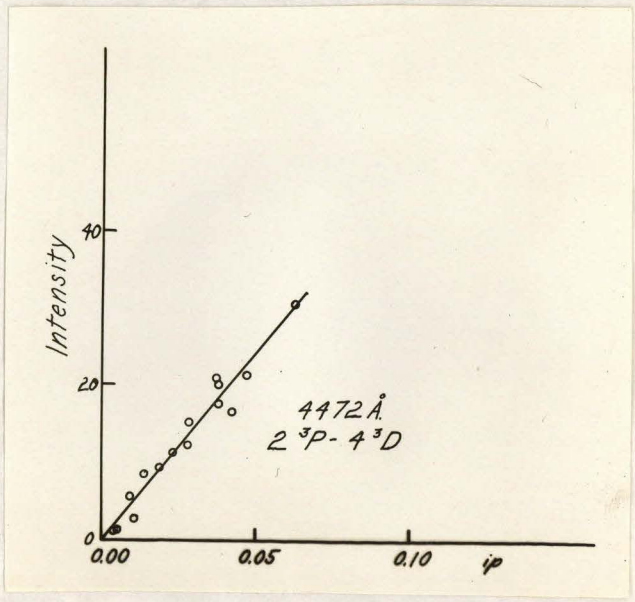

40
20
0
Intensity
4472 Å.
2 ³P - 4 ³D
0.00
0.05
0.10
ip

FIG. XI

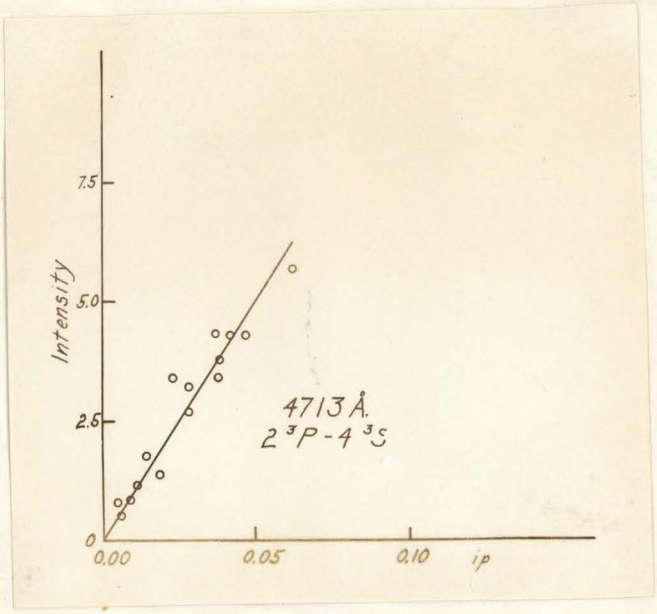


FIG. XII

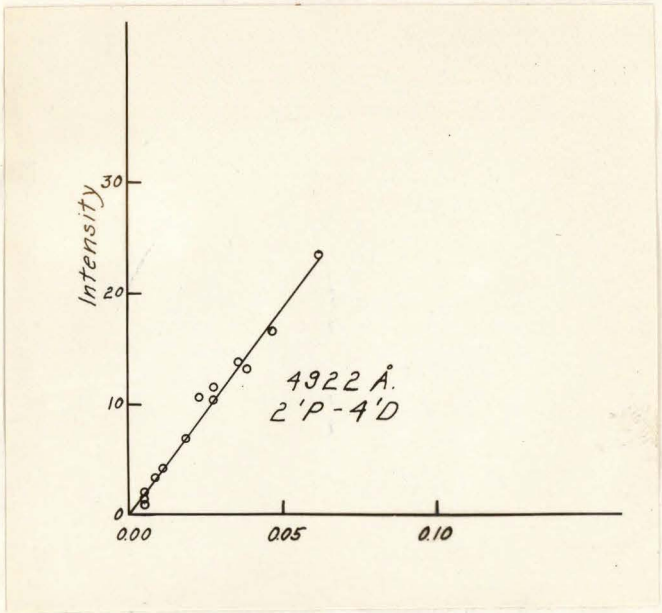


FIG. XIII

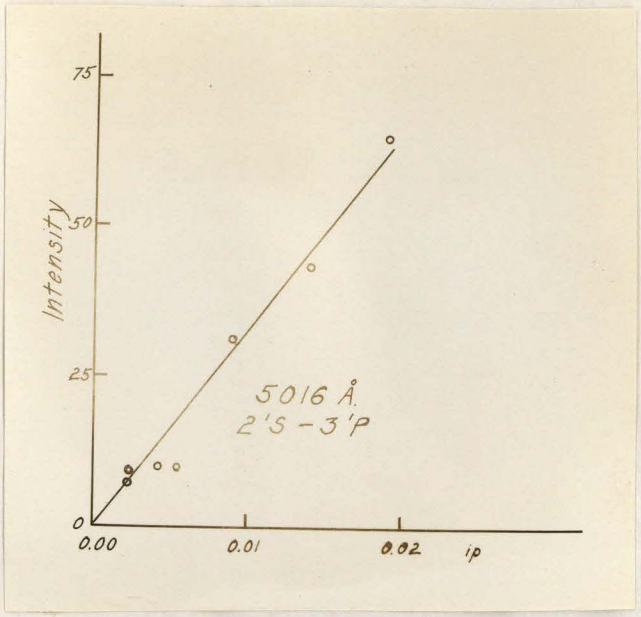


FIG. XIV

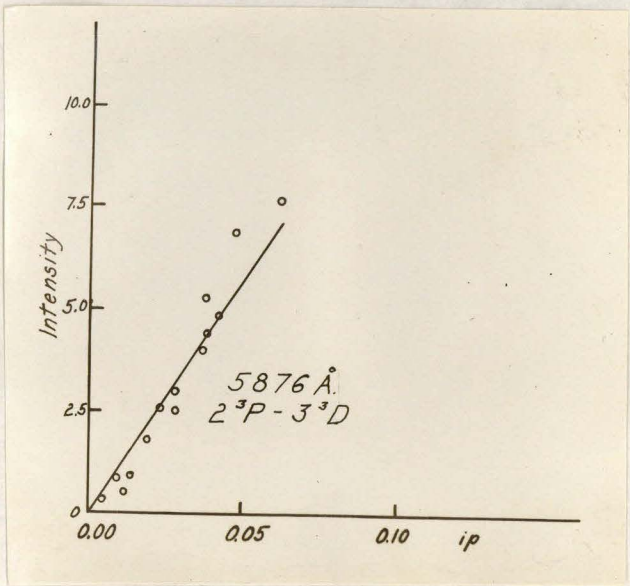


FIG. XV

(both of which may be present in small quantities) is deposited on the electrodes. The cleaning up action of the high velocity electrons would cause the removal of these impurities and therefore decrease the positive space charge present when the electrodes were coated. A search of the literature has failed to show sufficient data on the reflection of positive ions from dirty surfaces to indicate whether this explanation is correct.

6. Conclusions. The results of this research to date are twofold:

1.) It has been shown that by proper design of the discharge tube, it is possible to obtain an electron beam which is fairly homogenous, even with helium present. The homogeneity of this beam is shown by actual retarding potential tests which, when applied to tubes similar to those used in earlier work, show a striking departure from homogeneity.

2.) The linear relation between intensity and number of impacts, which has been established as a criteria for the proper conditions of excitation, has been satisfied and it is now possible, with the technique developed, to determine the excitation function of helium in a way which is independent of the pressure and current used.

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