IONIZATION OF GASES
BY POSITIVE ION BOMBARDMENT.

THESIS

by

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In Partial Fulfillment of the Requirements
for the Degree of
DOCTOR OF PHILOSOPHY.

California Institute of Technology
Pasadena, California
1929

INTRODUCTION.

The experimental work reported in this paper deals with a study of the problem of ionizing gases by the impact of slow positive ions using accelerating potentials less than 1000 volts. Definite evidence of ionization distinguished from other effects produced by the positive ions is submitted. The conditions of voltage, gas pressure, and collecting potentials are herein recorded, together with some estimate of the efficiency with which the positive ions ionize the gases used. In all of the present work a source of singly-charged potassium ions was employed to bombard successively hydrogen, nitrogen, argon, neon, and air. While the experimental conditions involve certain complications of quantitative interpretation which render impossible an accurate calculation of efficiencies from the results obtained with the tube utilized, yet the qualitative evidence of ionization is unambiguous; and under certain conditions of collecting potentials to be described later, the calculation of efficiencies should be reliable within approximately ten per cent.

An enormous amount of experimental work has been done upon the problem of ionization of gases by electrons since the early work of Lenard in 1913. This field has been so fruitful in yielding results of value in the development of spectroscopic theory that relatively little attention has been paid to the similar evidence of electric fracture of atoms by positive ion impact. The reasons for this condition of our present knowledge are several; among them are, i) the difficulty of getting an effective source of positive ions of sufficient intensity; ii) the relatively small efficiency of the ionization produced by the positives as compared to electrons; iii) the recognition of secondary effects which vitiate the early results obtained; iv) the difficulty of interpreting results, due chiefly to the large mass of the positive ions compared with electrons and their complex structure which together render the impact between + ion and gas molecule an exceedingly complicated occurrence.

When electrons ionize gas molecules and atoms, the chief consideration is one of <u>energy</u> transfer, and the simple equation of evergy loss in terms of radiation (the inverse photoelectric effect) is applicable. $Ve = \frac{1}{2}mv^2 = h\nu$. The question of the conservation of momentum is of minor importance in this case since the mass of the electron is so small in comparison with that of the atom struck. The electron can transfer virtually all of its kinetic energy (and momentum) to the ionized atom in an "inelastic collision." But when the impacting particle is an ion of mass comparable with, or greater than that of the atom struck, even though it may receive the same energy from the accelerating field as does the electron, it is evident from simple considerations of the conservation of momentum and of energy that the quantity of energy which it may transfer to an atom upon impact is, at best, only a fraction of its total kinetic energy. This fraction depends upon the nature of the collision in a calculable manner, but we have no way of knowing what the nature of the collisions is. The best we can do is to set a minimum value for the accelerating potential necessary to produce ionization by positives, with no assurance that we will be able to detect the few collisions which satisfy this minimum condition. A second consideration which appears to reduce the probability of ionization by positives is that the kinetic energy transfer upon impact must in some way be localized in a single electron of the atom which is ionized. This may be an event of relatively small probability in comparison with the number of times the positive ion transfers kinetic energy to the impacted atom as a whole. Furthermore, in order to ionize an atom by + ion bombardment, the electron which is liberated must escape from a greatly increased positive field due to the presence of the positive charge of the bombarding ion and to the field of attraction of its own parent atom. All three of these last considerations point to i) the appearance of ionization by positives at higher accelerating potentials than for electron ionization; ii) the lack of a clearly defined "ionizing potential" for positive ions; iii) relatively small efficiency of ionization by positives. Nowhere, in the present work was there found any evidence of the "breaks" due to radiation or double ionization such as are common in experiments on electron ionization. In no case was there found any certain evidence for ionization below 100 volts, which is several times the potential required for ~~an~~ electron ionization of the same gases. However, it is conceivable that some ionization below 100 volts might be detectable by the use of more sensitive measuring devices which would record the less probable impacts resulting in fracture of the atom. The theory of this type of ionization is still in a primitive state, dealing chiefly with considerations ~~of considerations~~ of conservation of energy and momentum and the (unknown) conditions of force fields about the colliding particles. 1,2,3,4.)

Mention should be made of the previous work in this field with some estimate of the results obtained.

1) Bahr and Franck5)(1914) using Lenard's method which had just been developed found what was supposed to be ionization below the potentials for electrons. This work has been generally discounted on the basis of secondary effects.

2) Pawlow6)(1914) used the same method in hydrogen and found ionization below 10 volts. This also has not been substantiated by later repetitions.

3) Horton and Davies7)(1919) attempted to ionize helium by positive ions from glowing tantalum and found no evidence for ionization up to 200 volts. They were the first to recognize the importance of the secondary effects, such as radiation and the secondary emission from metals.

4) Saxton8)(1922) believed he found ionization in H_2 by hydrogen positives below 18 volts. This has not been supported by later work (Hooper).

5) Dempster9)(1916) reports the excitation of light by positive rays as low as 5 volts! In some later work of his own10) he finds

no evidence of ionization by 900 volt protons in helium or hydrogen.

6) Tate[11)](1924) finds spectroscopic evidence of the ionization of mercury vapor by sodium positives between 40 and 70 volts. Mercury was ionized by Hg^+ at 70 volts.

7) Jones[12)](1927) excited mercury vapor by 1200 volt potassium positives. (Spectroscopic)

8) Hooper[13)](1925) carried on extensive experiments on hydrogen using sodium positives up to 925 volts without evidence of ionization.

9) Gurney[14)](1928) attempted to ionize hydrogen with 7000 volt potassium positives. The experiment led to inconclusive results.

For a summary and discussion of previous work in this field, see L. B. Loeb's paper in Science.[15)] It would appear that, with the exception of the spectroscopic evidence, little definite knowledge of ionization by positive ions has been found previously which did not have the taint of "secondary effects." None of these references deal with the range of potentials usually referred to as the "Canal Ray region" in which the positives certainly produce ionization since they have energy thousands of times the ionization potential values. We are concerned more particularly with the range below 1000 volts.

The effect of the impact of positive ions upon metal surfaces causing the emission of electrons has been studied by Klein[16)], Jackson[17)], Hyatt[18)], Oliphant[19)] and others. Any attempt to detect ionization in gases by positives must carefully exclude this effect or adequately account for it. It is believed that the present work separates ionization from secondary emission from metals in an unmistakable manner. A lesser effect, reflection of positives, has been investigated by Read[20), Gurney[21), and Oliphant[19). Evidence of its presence in this work is practically lacking and it may be considered throughout as negligible in amount.

It is essential to adjust experimental conditions so that any possible photoelectric effect due to the presence of excited atoms is ruled out. This may be done by the proper choice of collecting potentials. Furthermore, the collecting potentials should not be so great as to introduce the possibility of ionization by electrons. With a recognition of these secondary phenomena which may affect the results of experiment, the controlled conditions utilized throughout the major portion of this work were such as to exclude these effects, or at least to make them negligible in amount compared with ionization within the volume of the gas.

APPARATUS.

The tube used in these experiments was built in the Norman Bridge Laboratory after a design worked out by Mr. Max Wehrli and Dr. R. A. Millikan in 1924. It is schematically pictured together with its connecting system in Fig. 1. Several changes in the original electrode system have been made by the author as the necessities of the problem suggested.

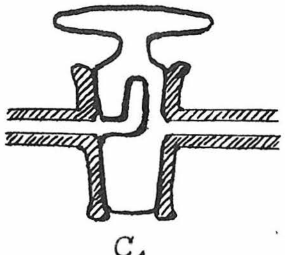
The source of positive ions was a platinum strip 1.2 x .3 cm resting in a cylindrical porcelain trough held rigidly between copper terminals. The platinum was coated with a few milligrams of oxide catalyst developed by C. H. Kunsman. All of the present work was done with the potassium source, the emission from which has been shown by Barton, Harnwell, and Kunsman22) to be practically pure potassium. After reducing the oxide in an atmosphere of hydrogen to obtain a good coating, the filament and cathode system was sealed to the rest of the tube. Not wishing to have the contamination of organic vapors enter into the tube, it was deemed best to seal the tube together in this manner without using a wax-joint although this made the necessary changing of filaments inconvenient. The filament was kept at fairly constant temperature by a heavy duty six-volt storage battery, the average current requirement being about 6.5 amperes to secure sufficient positive emission. A well coated filament was usually good for about 50 hours of operation, barring accidents, before the emission fell to an inconveniently low value. Unfortunately it requires a good many minutes for the emission current to become constant after closing the heating circuit; but it was found that, with the method of handling results utilized, wide variations in the filament emission did not appreciably affect the ratio of currents to the recording galvonometers. Emission currents of the order of one microampere were used in most cases; the positive current entering the ionization region in the upper part of the tube was of the order of 10^{-7} amperes, or less.

The entire filament system was enclosed in a hollow cylindrical cathode turned from a single piece of steel with a 2 mm hole in the top for the ion stream to enter the upper region of the tube under the accelerating potential, V_a. The source was placed approximately 2 mm from this hole. A 5 cm diameter nickel plate located just above the cathode served as the collector for the products of ionization. The ions were prevented from striking the collector, S, directly from the primary beam by means of a projecting ridge on the cathode which protruded through a hole in the collector. Situated approximately one centimeter above the collector plate was a wide-meshed grid of nickel wire inserted to control the potential within the space around it without offering much cross-section for the stoppage of ions and electrons. Above the grid a v-shaped nickel plate served to collect the positive ion stream; its shape was supposed to prevent the reflection of the positive ions. This element of design is rather unfortunate because reflection of positives is of minor importance, whereas the unsymmetrical field produced by the plate-grid system and the indeterminable volume between G and P from which the products of ionization are collected make the accurate calculation of the efficiency of ionization impossible. It should be beneficial to change the plate to a flat disc parallel to the grid and as close to it as convenient so as to reduce and make calculable the corrections necessary to account for ionization between grid and plate.

The electric connections are shown in Figure 2. It will be seen that the accelerating potential, V_a, which was supplied by a bank of small lead accumulators, could be varied continuously from zero to the highest values used, - about 1100 volts. V_a^+ was applied to the filament through the midpoint of a 30 ohm resistance. The total current in the space between F and C was measured by galvanometer G_1. This current, I_E, consists of the positive ion emission increased by any secondary emission of electrons from the cathode and by any ionization within the furnace. In general, less than 10% of the total emission from F passed through the hole in the cathode.

The collecting potentials on S and P could also be varied continuously and independently from zero to ± 150 volts, although these potentials, V_s and V_p, were in general maintained at values below 15 volts to prevent electron ionization from entering into the observed effects. It is important to note that nowhere in the region above the cathode are there any potentials applied which can give to electrons energy sufficient to ionize the gas, except in those cases where V_s and V_p were purposely raised above the ionizing potential of the gas being used. The currents to collector and plate, I_s and I_p, were measured by the two galvanometers, G_2 and G_3, of sensitivity approximately 10^{-10} amp/mm. By carefully working out the system of grounds and insulating the collecting potential batteries, it was possible to make wide variations of voltage on all three batteries without drift of the galvanometers. Whenever zero-drift was suspected due to change of potentials, a careful check of the zero readings was made immediately.

The gas-handling system used for neon and argon is shown in Fig. 1. The gases were obtained commercially in reasonable pure condition and were placed successively in the reservoir, R. A small amount of gas introduced into the bulb M was glowed for hours between magnesium electrodes attached to a 15,000 volt transformer; sputtering was continued until a good spectrum of the gas appeared. From M the gas was then passed into the experimental tube through the stopcock control C_1, C_2, and C_3. Stopcock C_4 was of special design suggested by Mr. Clancy for the introduction of small amounts of gas. The "pocket" within the head allowed the transfer of small quantities of gas with consequent facility in controlling pressure. A mercury cut-off, T, of the "suck-down" type was used to seal off the tube from the pumps when desired. This was operated by the two-way stopcock, C_0. Gas pressures were read on a MacLeod gauge whose connec-



C_4

tion entered the system on the pump side of the liquid air trap. Either liquid air or solid CO_2 were used on the trap during pumping and in the course of runs. The whole tube was baked out occasionally, particularly between runs with different gases.

The experiments with hydrogen and oxygen were carried out with commercial gases collected over P_2O_5 to insure dryness. Nitrogen was generated from sodium azide, NaN_3, after the method described by Tiede.23) A few grams of recrystallized sodium azide were placed in a side tube sealed to the reservoir system and after careful evacuation the azide was heated in a sandbath to 330°C. At this temperature decomposition begins with the emission of nitrogen in pure form; sodium is left deposited within the tube. The nitrogen was collected over P_2O_5 and admitted to the apparatus as needed.

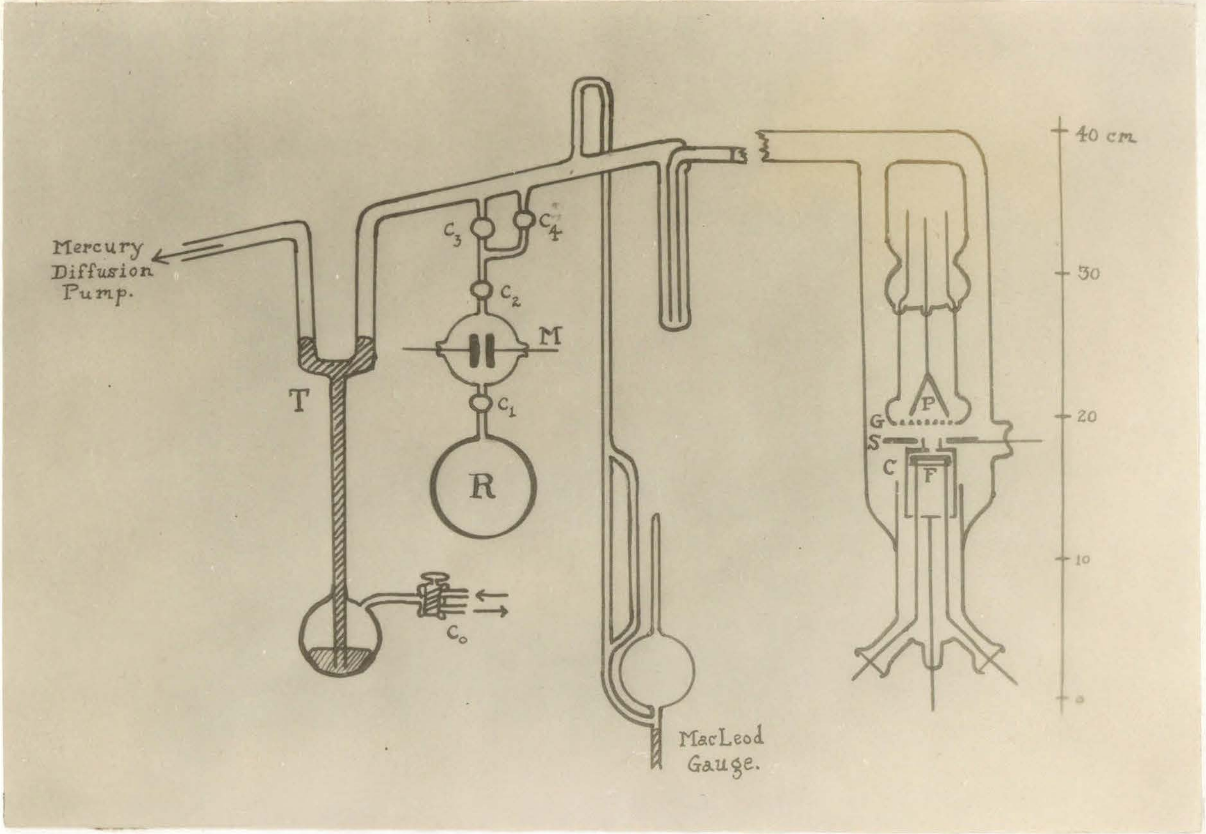


Figure 1. Experimental tube and its connections.

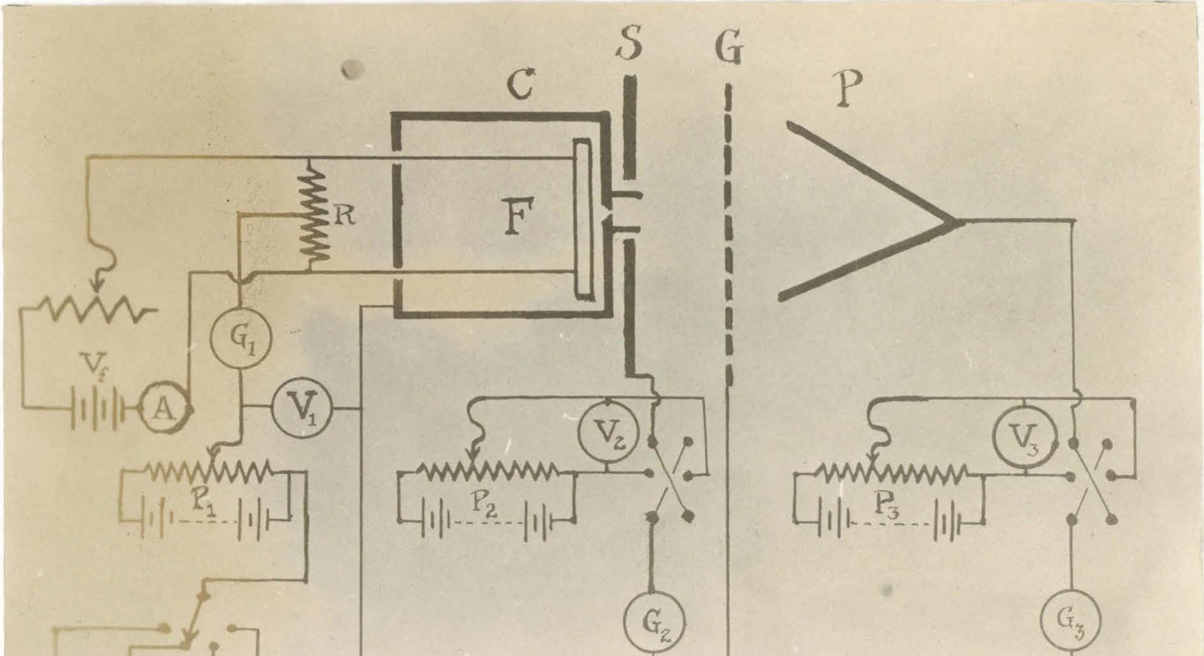


Figure 2. Electrical Connections.

METHOD OF HANDLING OBSERVATIONS.

There are three variable features in the operation of this apparatus for any one gas which may be utilized:

I) Variation of collecting potentials, V_s and V_p.

II) Change of Pressure within the tube.

III) Alteration of Accelerating Potential, V_a.

This suggests three types of runs which are significant in studying gases with this tube; i.e., variation of each of the previous factors while other conditions are maintained as constant as possible. All three modifications were used, although by far the greater part of the work was done with the third factor, V_a, as variable after the general characteristics of the phenomena of positive ion bombardment were understood from a study of I) and II). In any case, the observations consist in recording the currents received upon collector and plate, I_s and I_p, together with the gas pressure, accelerating potential, collecting potentials, and filament current at the time. In the latter part of the work the total emission current, I_E, was also recorded by galvanometer G_1 in order to study more carefully the conditions within the furnace. It was suspected that a glow discharge might be occurring unobserved within the furnace at the pressures and potentials used, affecting the accuracy of results and causing suspicion of a strong photoelectric effect which might prevail. This suspicion has been shown to be groundless, although the emission from the filament is undoubtedly affected by the presence of gas in a manner which needs careful study. It is likely that the observations of Barton, Harnwell, and Kunsman22) regarding the emission from catalyst-coated filaments are not perfectly valid when gas is present around the filament.

It is essential to analyze the currents arriving upon S and P for any particular set of conditions of collecting potentials and gas pressure, since variations in the ratio of these currents occur with changes in the values of V_s and V_p; and inasmuch as the evidence for ionization is based upon these ratios, we should be able to interpret any change which occurs due to change of conditions in the tube. This has not always been possible to do in a quantitative manner because of the design of the tube, but it is comparatively easy to make a qualitative interpretation of results.

I. VARIATIONS IN COLLECTING POTENTIALS. ACCELERATING POTENTIAL CONST.

A. Plate Positive.

1. Collector Positive: $V_s > V_p$

This proved to be the most easily interpreted condition and it is the one which was used in most of the work under heading III. In order to isolate the phenomenon of ionization, due account must be taken of the secondary effects of electron emission from metals due to positive ion bombardment, photoelectric emission due to the presence of excited atoms, and reflection of positives. In order to eliminate these effects as far as possible, the plate was usually maintained slightly positive with respect to the grid (ground), and the collector was kept more positive than the plate. Thus, electrons could not escape from the plate nor from the region between the plate and grid to the collector. The slightly greater positive potential of S kept any positive ions from reaching S by reflection from the plate or by stoppage of the incident ions from the filament between G and P due to collisions with gas atoms. Hence S collected only such electrons as were liberated from the gas between S and G, together with any liberated from the grid by secondary emission. The latter were small in amount, as may be seen from data taken at low pressures where collisions between gas atoms and positive ions were rare. (See Fig. 6-9)

The ratio of the electron current, I_s, to the positive ion current, I_p, was taken as a close approximation to the number of ions formed per positive ion within the region S-G at any particular pressure and accelerating potential. Actually, both I_s and I_p are subject to corrections. As already mentioned, I_s consists of electrons from the gas and secondary electrons from the grid.

$$\bar{I}_{\text{ionization}} = I_s \text{ (observed)} - \bar{I}_{\text{sec. emission.}} \qquad (1)$$

The last term can be found from runs taken at low pressure ($<$ .0001 mm). The correction to I_p is not so simple, and the design of the tube does not permit of an exact correction being made. I_p consists of initial positive ions arriving on the plate from the filament, diminished by electrons liberated from the gas between G and P, and also diminished by any reflected positives leaving the plate to discharge through the grid to ground. Furthermore, some of the initial positive ions may lose too much energy in passage through the gas to reach the plate against the retarding potential, V_p^+. The number of ions stopped within the gas cannot be exactly calculated unless an assumption is made that the same per cent of the total emission passes through the hole from the filament at high pressures as at low.

$$I^+_{\text{initial}} = I_{p(\text{obs})} + I^-_{\text{ionization}} + I^+_{\text{refl.}} + I^+_{\text{scattered}} \qquad (2)$$

The first correction term is approximately calculable on the assumption that the positive ions are as effective ionizers above the grid as below. Then, $I^-_{\text{ionization}} = kI_s$, where $k = \frac{\text{vol. G-P}}{\text{vol. S-G}}$, approximately 3 for this apparatus. The next term seems to be negligible in amount, as may be seen by making V_s negative and attempting to collect reflected positives at low pressure. The last term is not accurately known, but judging from the ratio of I_p / I_E at various pressures, it is not a very large factor until pressures above .7 mm are reached. It then mounts rapidly in importance as the gas becomes more and more "opaque" to the positive ions.

Neglecting the last two terms of Eq. 2, we can get a fairly close approximation to the ratio I^-/ I^+ in terms of observable galvanometer currents:

$$\frac{I^-}{I^+} = \frac{I_{s(\text{obs})} - I^-_{\text{sec. emiss.}}}{I_{p(\text{obs})} + kI_{s(\text{Obs})}}, \text{ approximately: } \frac{I_{s(\text{obs})}}{I_{p(\text{obs})} + kI_{s(\text{Obs})}} \qquad (3)$$

2. $V_p > V_s > 0$. Collector still positive.

Where V_s is less than V_p, the ratio of I_s / I_p changes rapidly. The calculation of corrections is complicated by the fact that an unpredictable fraction of the positive ions formed or scattered between G and P succeed in reaching the collector S. An approximation utilizing the relation between V_p and V_s gives only partial success in interpreting results.

$$\frac{I^-}{I^+} = \frac{I_{s(obs)}\left\{1+k(1-V_s/V_p) - I^-_{sec.\ emiss.}\right\}}{I_{p(obs)} + k\, I_{s(obs)}} \qquad (4)$$

3. Collector Potential Negative.

When V_s is negative, V_p positive, the interpretation of the ratio I_s/I_p is not so clear as in Case 1). S now collects <u>positive</u> ions. All positives formed by ionization throughout the whole volume S-P, plus positives from the initial beam which have been retarded too much to reach P, plus reflected positives,--all reach the collector. I_p now consists of those positives from the original beam which succeed in reaching P, diminished by reflected positives and by all electrons released from the gas by ionization. The ratio I_s/I_p consequently increases materially and appears to be very sensitive to slight changes in gas pressure. This increase may be seen in <u>Fig. 3</u> in the case of air at .65 mm pressure, V_p + 10 volts, and V_s ranging from +50 to -50 volts. To obtain the true $\frac{I^+_{ionization}}{I^+_{initial}}$ when S is negative, we analyze I_s and I_p as follows:

$$I_{s(obs)} = I^+_{ionization} + I^+_{scattered} + I^+_{refl.} \qquad (5)$$

$$I_{p(obs)} = I^+_{initial} - I^-_{ionization} - I^-_{sec.\ em.\ from\ grid} - I^+_{refl.} \qquad (6)$$

Neglecting scattering from the primary beam and the minor items of secondary emission from the grid and reflection of positives from the plate, we have a fair approximation:

$$\frac{I^{+}_{\text{ionization}}}{I^{+}_{\text{initial}}} = \frac{I_{s(\text{obs})}}{I_{p(\text{obs})} + I_{s(\text{obs})}} \tag{7}$$

This ratio should be roughly <u>four times</u> as great as the ratio I^{-}/I^{+} found for $V_s > V_p$, since the whole volume S-P is approximately four times the partial volume, S-G from which electrons were collected in the previous case.

B. Plate Potential Negative.

1. V_s Positive.

When the plate potential is made negative, secondary emission from the plate enters as an important correction to the current received on the collector. With no gas present, one collects secondary electrons on S so long as V_s is positive. I_p consists in the initial primary beam of positives, increased by the amount of secondary emission. Under these conditions a rough check can be made on the experiments on secondary emission at low pressure and the efficiency for this plate can be calculated.

$$f = I^{-}/I^{+} = \frac{I_{s(\text{obs})}}{I_{p(\text{obs})} - I_{s(\text{Obs})}} \tag{8}$$

When gas is admitted, S now collects the electrons liberated from the whole volume of gas between S and P in addition to the secondary electrons from grid and plate. I_p consists in the primary beam, increased by the secondary emission and by the positive ions liberated from the gas.

$$I^{-}_{\text{ionization}} = I_{s(\text{obs})} - I^{-}_{\text{sec. em.}} \tag{9}$$

The latter term is calculable from low pressure observations = f I_p^+.

$$I^+_{initial} = I_p(obs) - I^-_{sec.\ em.} - I^+_{ionization}. \qquad (10)$$

These last two correction terms are, however, nothing but the observed I_s. Hence, to good approximation the correct ratio for ionization is:

$$\frac{I^-}{I^+} = \frac{I_s(obs) - f\ I_p(obs)}{I_p(obs) - I_s(obs)} \qquad (11)$$

in which "f" is the secondary emission factor determined at low pressure.

2. $0 > V_s > V_p$. Both V_s and V_p negative.

This is a transitional region in which the ratio I_s/I_p changes rapidly. With the present tube it is difficult to interpret the ratio quantitatively with accuracy. The ratio decreases since the collector now begins to receive positive ions from the space S-G and also retards some of the electrons from above the grid. Finally V_s becomes sufficiently negative so that the positive ion current predominates and the ratio I_s/I_p changes sign.

3. $|V_s| > |V_p|$ Both negative.

V_s now prevents any electrons liberated above G from reaching S. I_s becomes pure positive ion current due to positives liberated between S and G, plus any from the primary beam which are sufficiently retarded by collision to be affected by the field of the collector. I_p represents those positives which get through to the plate from the filament (practically all of them, since V_p helps them along), plus positive ions formed above the grid by ionization, plus secondary emission from the plate, the current from which must go out on the grid.

$$I^{+}_{\text{ionization}} = I_{s(\text{obs})} - I^{+}_{\text{scattered}} \quad \text{(Collected from region S-G)}$$

$$I^{+}_{\text{initial}} = I_{p(\text{obs})} - k\, I^{+}_{\text{ionization}} - I^{-}_{\text{sec. em.}}$$

The last term of the previous equation is approximately calculable as

$$I^{-}_{\text{sec. em.}} = f\, I_{p(\text{obs})}$$

This correction is good for reasonably low gas pressures when I_p is composed chiefly of initial ions from the filament. A fair approach to the correct ratio for ionization in this case is then:

$$\frac{I^{+}_{\text{ionization}}}{I^{+}_{\text{initial}}} = \frac{(1 + f)\, I_{s(\text{obs})}}{I_{p(\text{obs})} - k\, I_{s(\text{obs})}} \tag{12}$$

No specific mention has been made regarding photo-electric effect upon the metal parts. This correction may be included in most cases under the heading of "secondary emission," except that it may be dependent upon gas pressure whereas the secondary emission was assumed not to be.

The foregoing analysis of currents and their ratios for various collecting potentials has been given considerably in detail in order to show what the characteristics of the apparatus are. <u>Figs. 3 and 4</u> show how the ratios vary for a particular case when air was used under an accelerating potential of 550 volts and .65 mm pressure so that ample ionization would be detectable. It would be a tedious process to repeat these curves for every gas pressure and accelerating potential desired, since a large number of observations are represented in each case. Consequently, most of the work was done with constant collecting potentials, $V_s > V_p$, with both <u>positive</u> as analyzed in Case I A 1.

II. VARIATION OF PRESSURE. COLLECTING AND ACCELERATING POT'L CONST.

A few runs of this type were taken in order to determine at what pressure the effect of ionization set in. No appreciable ionization was found below .1 mm in general, a fact which is remarkable when one turns to mean free path considerations. This point will be discussed at length in a later section of this paper. Fig. 5 shows the characteristic observations taken in this type of run. The chief information to be gained concerns the range of pressure through which the effect is present. A great many curves of this type could be compounded from chosen data in a large number of runs taken under III.

III. VARIATION OF ACCELERATING POTENTIAL. V_s, V_p, AND PRESSURE CONST.

The most systematic method of measuring ionization was to set the collecting potentials at chosen values and vary the accelerating potential, V_a, from zero to the maximum value which was usually 750 volts; in a few cases, potentials to 1100 volts were used. Care was taken in adjusting the zero readings of the galvanometers and efforts were made to detect the first trace of ionization. Since the currents to the collector were feeble, it was not always possible to locate the exact inception of ionization although it never appeared below 100 volts. As V_a was increased above 100 volts, I_s increased also. In the previous analysis when V_s and V_p were both positive, the currents to the collector were shown to be as free as possible from secondary phenomena. Hence most of the results for the gases studied were based upon this system of potentials, with $V_s > V_p$.

After changing V_a by steps from zero to 750 volts, the pressure was altered and the process repeated. Several curves were plotted on this basis for each gas at different pressures, as in Figs. 6-9, clearly showing how the ratio of I^-/I^+ increases with increasing pressure and V_a. The lowest curves are those taken when the pressure was too low for ionization to play any important part; hence they represent the part played by secondary emission from the grid. These curves have been corrected according to Eq. 3.

In order to reduce these various curves to a comparable basis, the method suggested by Compton and Van Voorhis[24)] was utilized. The values of the ratio I^-/I^+ for each curve were divided by the pressure in millimeters of mercury and by the distance in centimeters over which the products of ionization were collected, thus giving the number, N, of fresh ions formed per initial positive ion per centimeter path at one millimeter pressure.

$$N = \frac{I^-_{\text{ionization}}}{P \times L \times I^+_{\text{initial}}} \tag{13}$$

For the case where the ions were collected only from the region between collector and grid, L was approximately one centimeter. This number, N, may be called the "efficiency of ionization." The values calculated in this way may be several per cent <u>high</u>; they are not likely to be too low. The reason for this lies in the fact that the true value of I^+_{initial} which produces the ionization cannot be accurately determined on account of scattering, and the observed value is probably too low, making N too large. Another correction term of unknown value is that of ionization produced by <u>neutral</u> atoms which started as K+ ions and were neutralized after having fallen through all or part of V_a. Theoretically, such fast moving atoms would be better ionizers than positive ions moving with the same velocity, but they would not be recorded in I_p.

A few additional remarks may clear up certain points of procedure:

1. The grid and cathode were always maintained at zero potential.

2. All calculations of efficiencies have been corrected for the difference in galvanometer sensitivities on G_2 and G_3.

3. So long as $V_s^+ > V_p^+$, wide variations in V_s both positive and negative appear to have no effect upon the positive ion current to the plate when no gas is present. Evidently the + ion stream is not accelerated or retarded by V_s, due no doubt to an equipotential "core" between the ridge on the cathode and the grid through which the ion beam passes. When gas is present there is sufficient scattering and retarding of the positive ions to throw some of them into control of V_s.

4. So long as $V_a + > \pm V_p$, the current to P is unaffected by wide variations in V_p, both positive and negative, with no gas present.

5. The total filament emission appears to be reduced a few per cent by the presence of gas, after a slight increase when the gas is first admitted. This reduction is perhaps due to a slight temperature decrease caused by conduction of heat from the filament by the gas. The decrease is contrary to what would be expected if ionization within the furnace were occurring to any

appreciable extent.

6. The ratio I_s/I_p for $V_s^+ > V_p^+$ is essentially independent of the value of I_p: an increase in I_p of one-hundred fold changes the ratio by only 3%. Hence small changes in the emission do not affect the results materially.

7. The practical limit of sensitivity of the apparatus as used was approximately .001; i.e., currents to S less than .001 those to P could not be detected. An electrometer in place of G_3 would increase this sensitivity.

RESULTS.

I. VARIATION OF COLLECTING POTENTIALS.

To illustrate the analysis undertaken on pp. 14-20, curves are given in Figs. 3 and 4 showing the measured I_s/I_p for Air at .65 mm pressure with V_a constant at 550 volts, together with curves taken under the same conditions of potential but with the gas pressure below .0001 mm. The corrections indicated in the previous pages have been calculated for this case and are recorded in the following tables. Greater reliance is placed upon the accuracy of the experiment when V_p is positive than when it is negative; the ratio in the latter case is undoubtedly too large. With a different placement of the Plate, as mentioned previously, better corrections to the V_p^- case could be made. It will be seen that the latitude of variation in the ratio I_s/I_p is greatly reduced in the corrected ratios; and although not all that might be desired, the corrections applied appear to work consistently in the right direction. The small rise in I^-/I^+ at ± 50 volts may be due to ionization by electrons.

TABLE I.

V_p = +10 v. V_a = 550 v. Pr. = .65 mm Air.

V_s	I_p	I_s	I_s/I_p	I_s/I_p corrected	Correction applied.
50	10.5	1.6	.152	.096	Eq. 3
25	5.9	.7	.119	.080	"
15	10.2	1.2	.118	.080	"
10	6.5	.7	.108	.076	"
5	5.9	.4	.068	.141	Eq. 4
- 5	14.9	-7.0	.47	.080	Eq. 7
-25	8.4	-5.55	.66	.099	"
-50	9.6	-6.65	.69	.102	"

TABLE II.

V_p = -10 v. V_a = 550 v. Pr. = .65 mm Air.

V_s	I_p	I_s	I_s/I_p	I_s/I_p corrected	Correction applied.
50	23.4	6.3	.269	.228	Eq. 11
25	14.6	3.3	.226	.174	"
15	20.2	4.5	.223	.168	"
10	16.8	3.5	.208	.148	"
-15	16.3	-1.6	.098	.153	Eq. 12
-25	14.7	-1.4	.095	.147	"
-50	20.2	-2.4	.118	.203	"

II. VARIATION OF PRESSURE.

In Fig. 5 are some collected results for argon, neon, nitrogen and air, showing the ionization as a function of gas pressure with V_a chosen at 750 volts so as to insure sufficient ionization. As will be seen from the curve, little measurable effect appears for pressures lower than .1 mm, a result which is striking from the viewpoint of kinetic theory since the expected mean free path of the ions is so short at these pressures where the effect of ionization appears. This will be discussed in the next section.

Pressures were used in a few instances above 1 mm, but most of the work was carried out between .1 and .7 mm. Above .7 mm the gas seems to scatter the initial beam very strongly and I_p falls off rapidly as may be shown by the decrease in the ratio I_p/I_g. Furthermore, at the higher pressures there was greater danger of arcing at the potentials used, with consequent hazard to the sensitive instruments. A few mishaps occurred on this account.

III. VARIATION OF ACCELERATING POTENTIAL, V_a.

The collected results of a large number of runs in various gases are shown in Figs. 6, 7, 8, 9. The corrected ratio I_s/I_p is plotted as a function of V_a for a number of pressures in each gas. All of these results were obtained with $V_p \cong +10$ volts, $V_a \cong +15$ volts; the correction applied is the one derived on Page 13, Eq. 3. There is a great similarity between the results for different gases as far as general characteristics of the effect are concerned; the chief difference lies in the numerical values of I_s/I_p for the various gases used when compared at the same pressure and accelerating potential. The curves for Argon indicate that the maximum efficiency is not far above 750 volts.

HYDROGEN.

Hooper13), Gurney14), and some of the previous workers attempted to ionize Hydrogen by positive ions without success. They all worked at far lower pressures than those used in these experiments, so it was of interest to see whether H_2 could be ionized in this tube under the conditions which yielded unmistakable ionization in Neon and Argon. The results were negative, and although pressures as high as 1.2 mm were used and accelerating potentials up to the arcing voltage were applied, no ionization could be distinguished from secondary emission from the grid.

The collected results of the efficiency of ionization, N, caused by K+ ions in those gases studied are shown in Fig. 10 These curves are calculated from the curves shown in Figs. 6-9 according to Eq. 13, duly averaged. Comparing these values of N with those obtained by Compton and Van Voorhis[24)], we see that ionization by positives is far less efficient than by electrons. None of the values of "N" in Fig. 10 have reached a maximum at 750 volts, whereas electron ionization passes through its most efficient values at far lower voltage. In the following table are given the values for $N^-_{max.}$ for electron bombardment at the potential for the maximum, together with the value of N for K+ bombardment in the same gases at 750 volts. The relative efficiencies of the two processes will readily be seen, that for 750 volt K+ ions being in every case less than 4% of that for electron ionization at the respective maxima for the various gases.

TABLE III.

Gas	$N^-_{max.}$	$V_{max.}$	N_{750} (K+)	$N^+_{750}/N^-_{max.}$
Argon	10.33	140	.288	.028
Neon	3.22	340	.112	.035
Nitrogen	9.96	175	.124	.013
Hydrogen	3.55	145	None	o

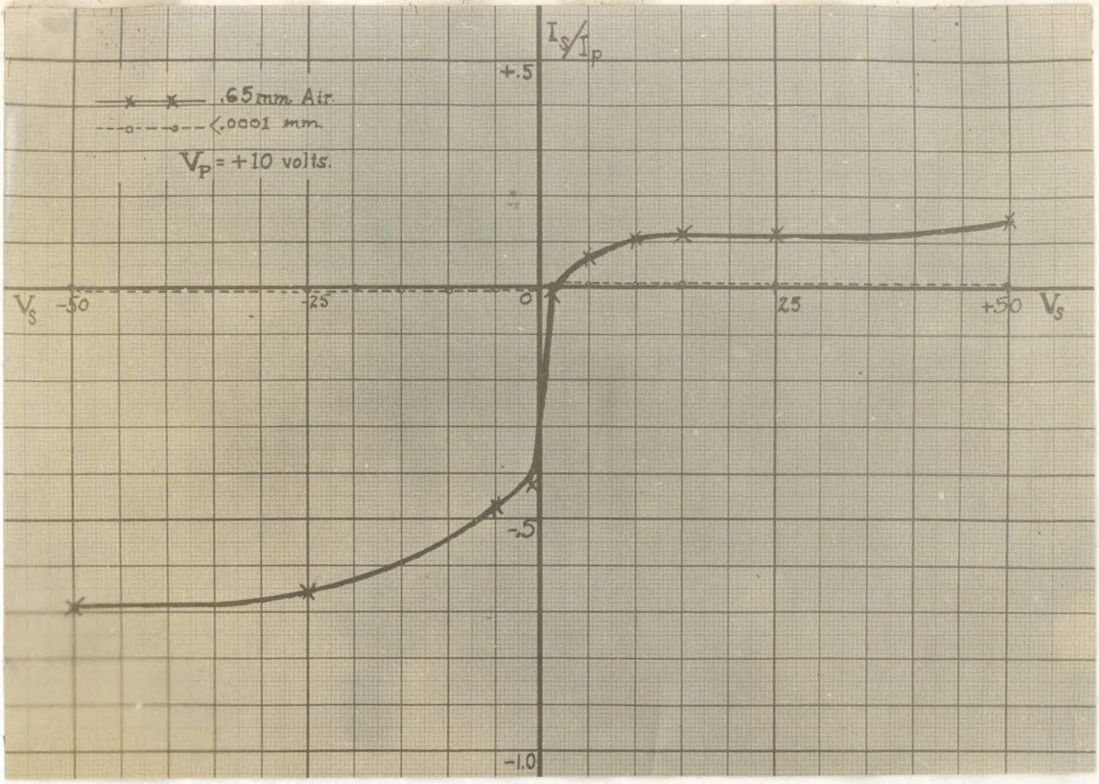


Figure 3. Variation in I_s/I_p with change in potential of the collector. $V_p = +10$ v. $V_a = 550$ v. Pressure = .65 mm Air.

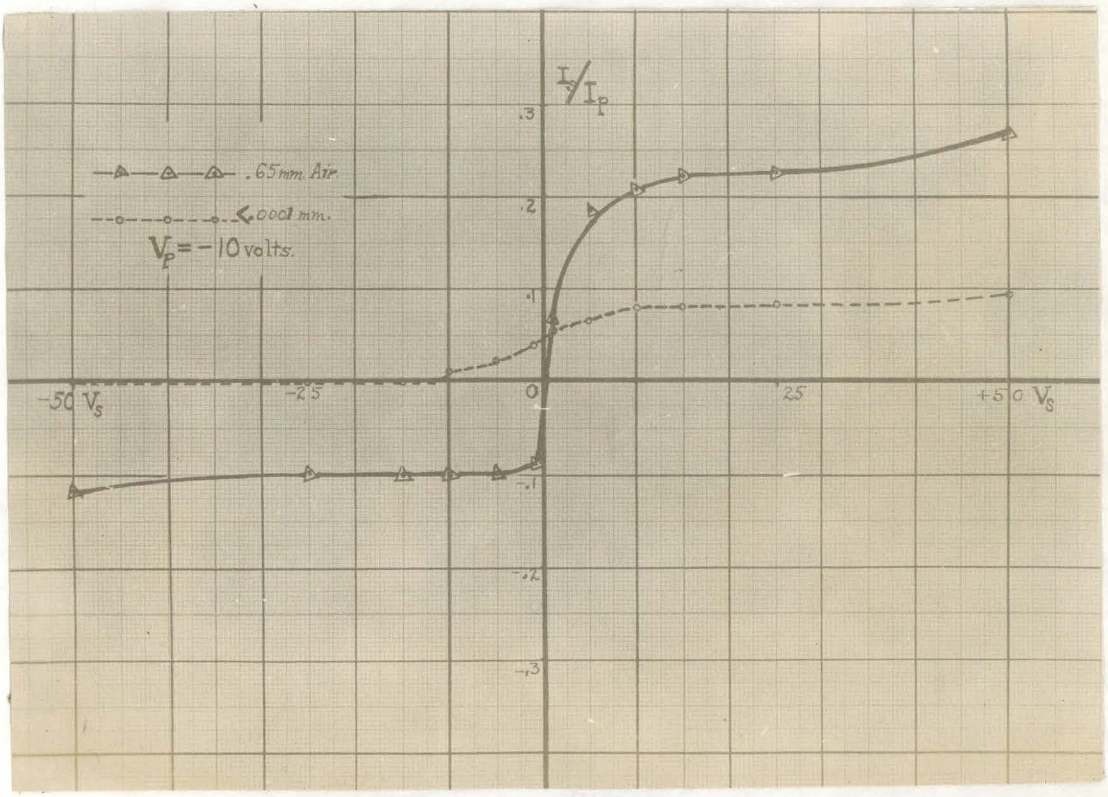


Figure 4. Variation in I_s/I_p with change in potential of the collector. $V_p = -10$ v. $V_a = 550$ v. Pressure= .65 mm Air.

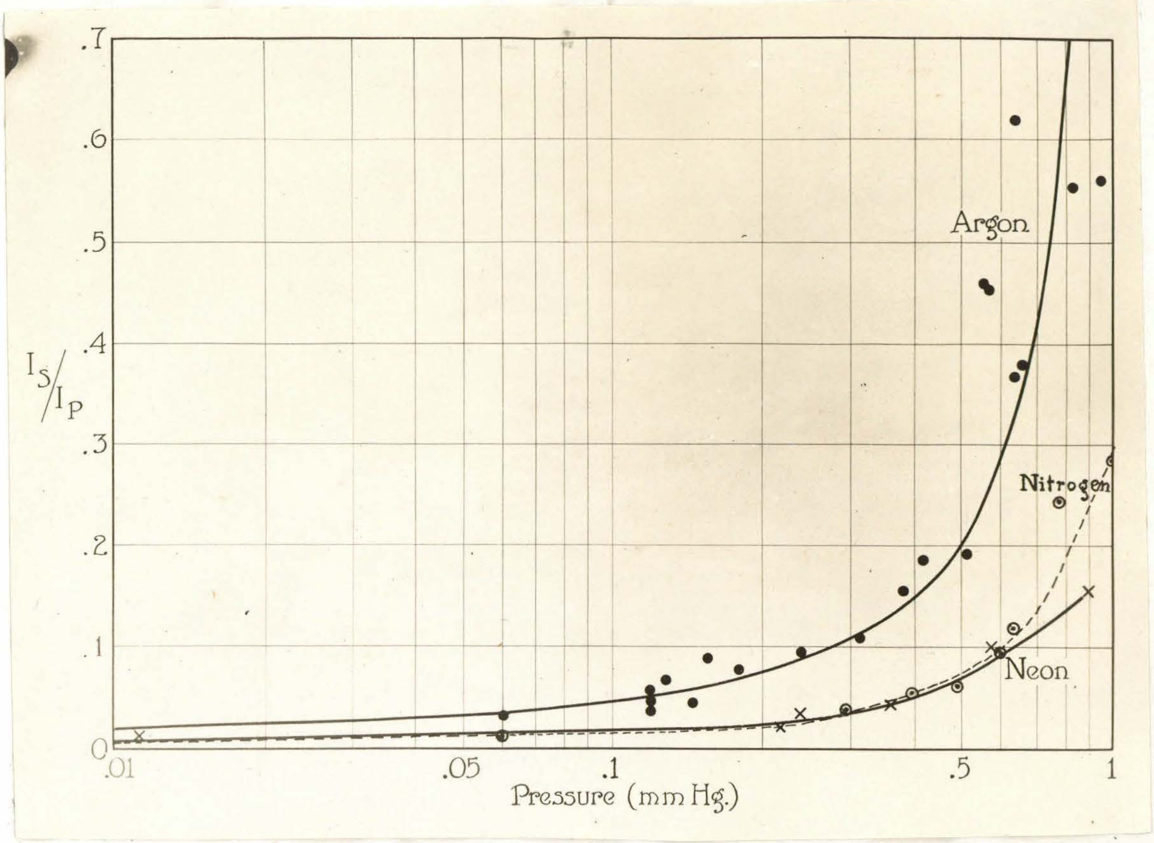


Figure 5.

Variation of ionization in neon, argon, and nitrogen plotted against the log of gas pressure.

I_s/I_p has not been corrected in this case for ionization occurring above the grid. A similar graph for air would appear very close to that for nitrogen.

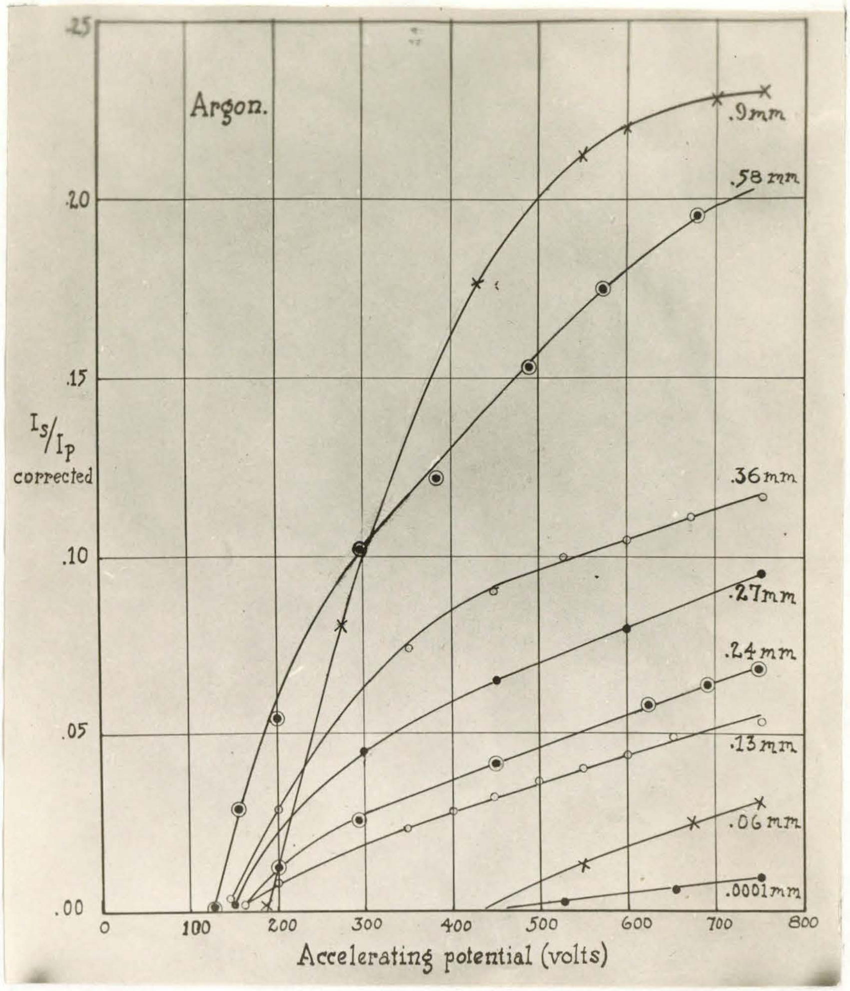


Figure 6.

Ionization in argon at several selected pressures, plotted against the accelerating potential.

I_s/I_p has been corrected in each case shown in the curves of Figs. 6-9 according to Eq. 3.

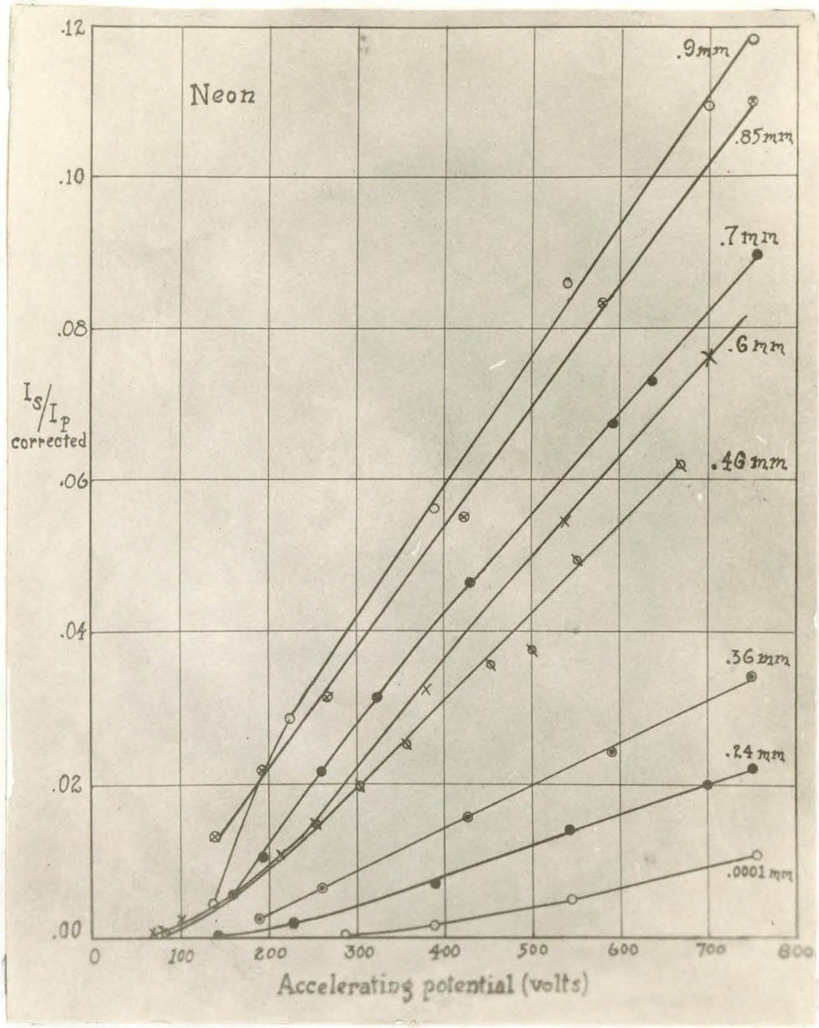


Figure 7.

Ionization in neon at several selected pressures, plotted against the accelerating potential.

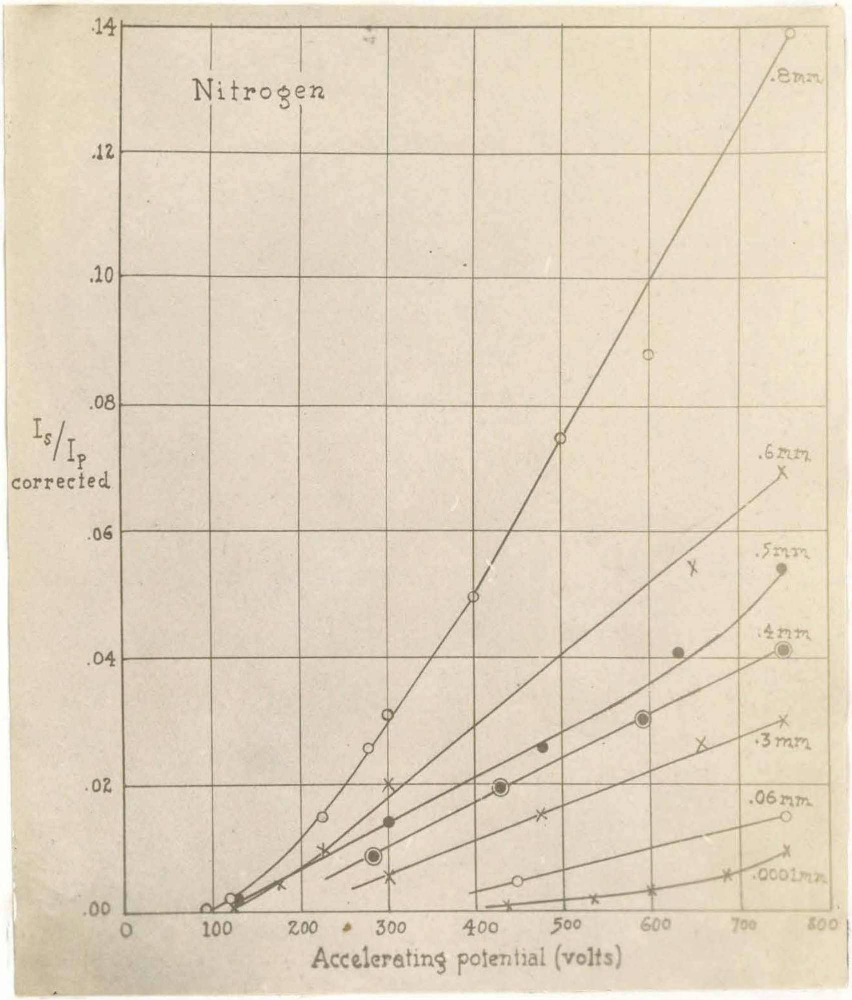


Figure 8.

Ionization in nitrogen at several selected pressures, plotted against the accelerating potential.

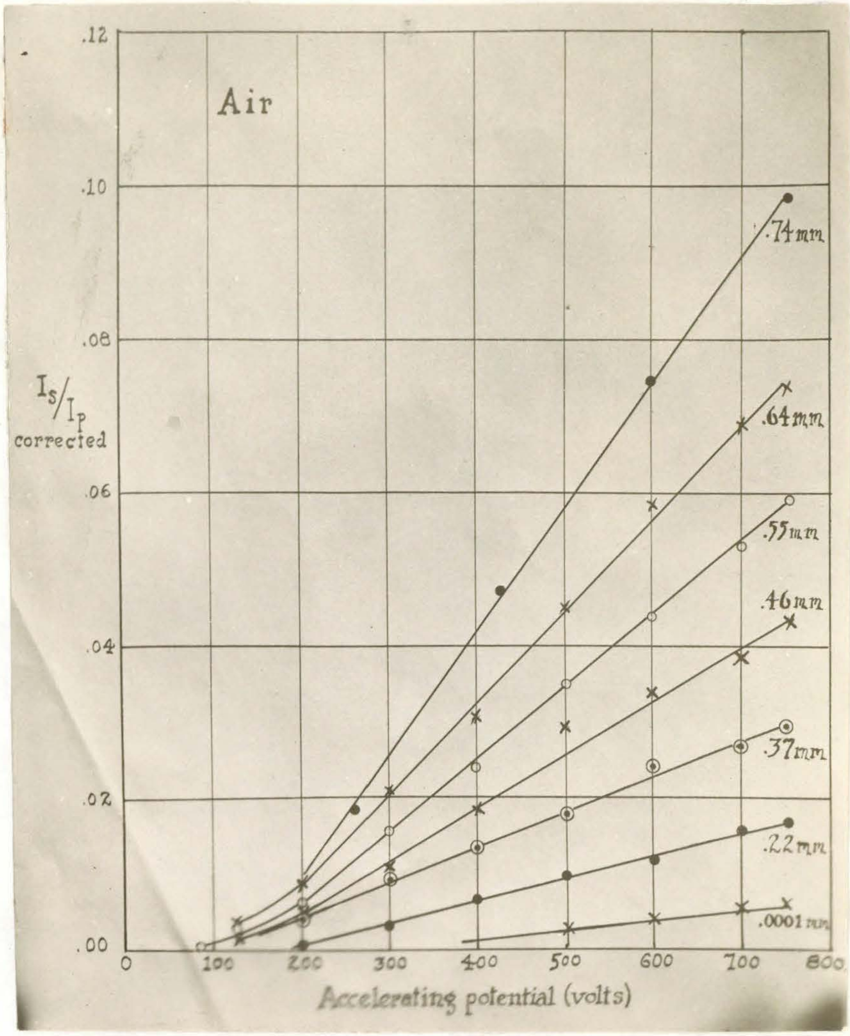


Figure 9.

Ionization in air at several selected pressures, plotted against accelerating potential.

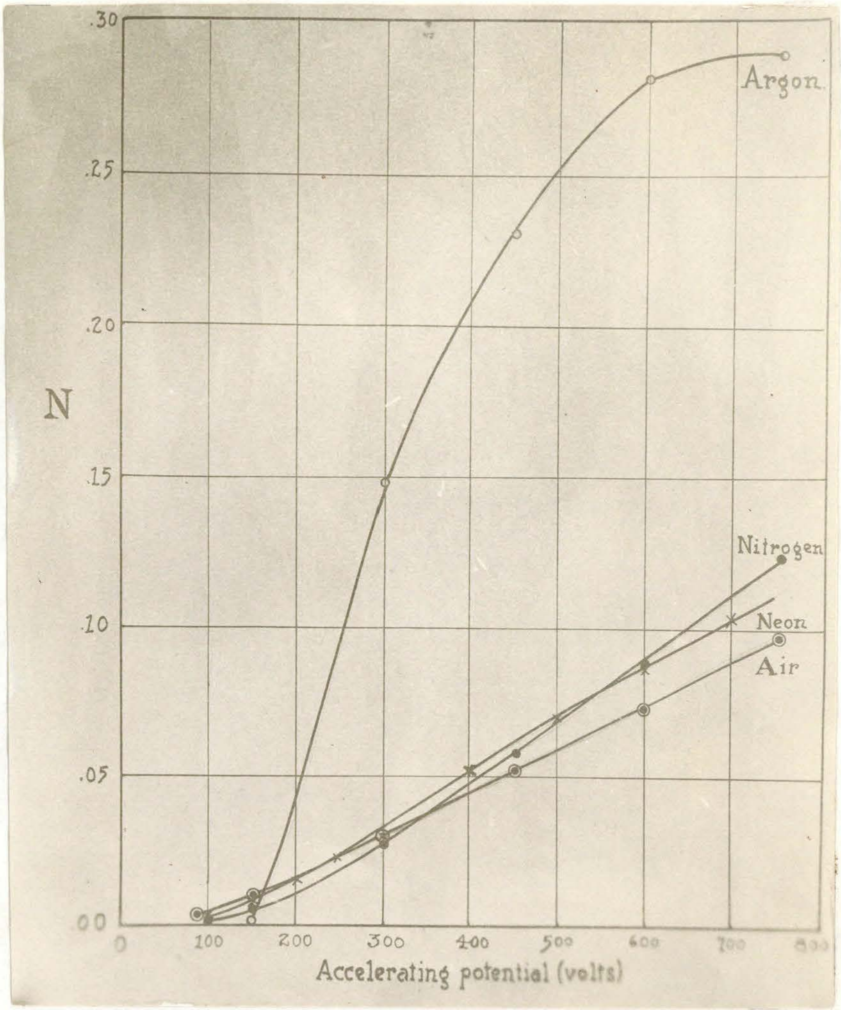


Figure 10.

Plot of N, the number of ions formed per initial positive ion per centimeter path, reduced to 1 millimeter pressure for argon, neon, nitrogen, and air.

These curves are calculated from the curves of Figs. 6-9 together with a number of similar curves according to Eq. 13.

VALIDITY OF RESULTS.

In the section on Method of Handling observations, a considerable amount has been said concerning the treatment of secondary effects. One further curve is given in Fig. 11 showing the amount of secondary effect present in the ratio I_s/I_p at low pressure under three conditions: 1) plate negative, collector positive, so as to collect secondary electrons from grid and plate on S; 2) plate positive, collector negative, so that collector receives only reflected positive ions (less than 1% so long as $V_a > V_p$); 3) both plate and collector positive, as actually used in the entire portion of the work shown in Figs. 6-9. The dotted line (3) in Fig. 12 shows the part played by secondary effects,- almost a negligible amount. The reasonable assumption is made that this secondary emission (with the exception of that due to photoelectric effect) is a maximum at low pressures.

There are three other items which deserve consideration in this critique of results: 1) Collisions of the Second Kind; 2) Photoelectric Effect; 3) Metastable atoms. The first has been studied for positive ion collision by Harnwell[25]; it is the effect observed in a mixture of gases of different ionization potentials wherein a metastable atom may ionize another atom whose ionization energy lies below that of the energy of excitation of the metastable atom. The effect may be ruled out so long as the gases dealt with are pure. Also, the energy liberated upon neutralization of a K+ ion is not sufficient to ionize any of the gases used in these experiments. Second, any

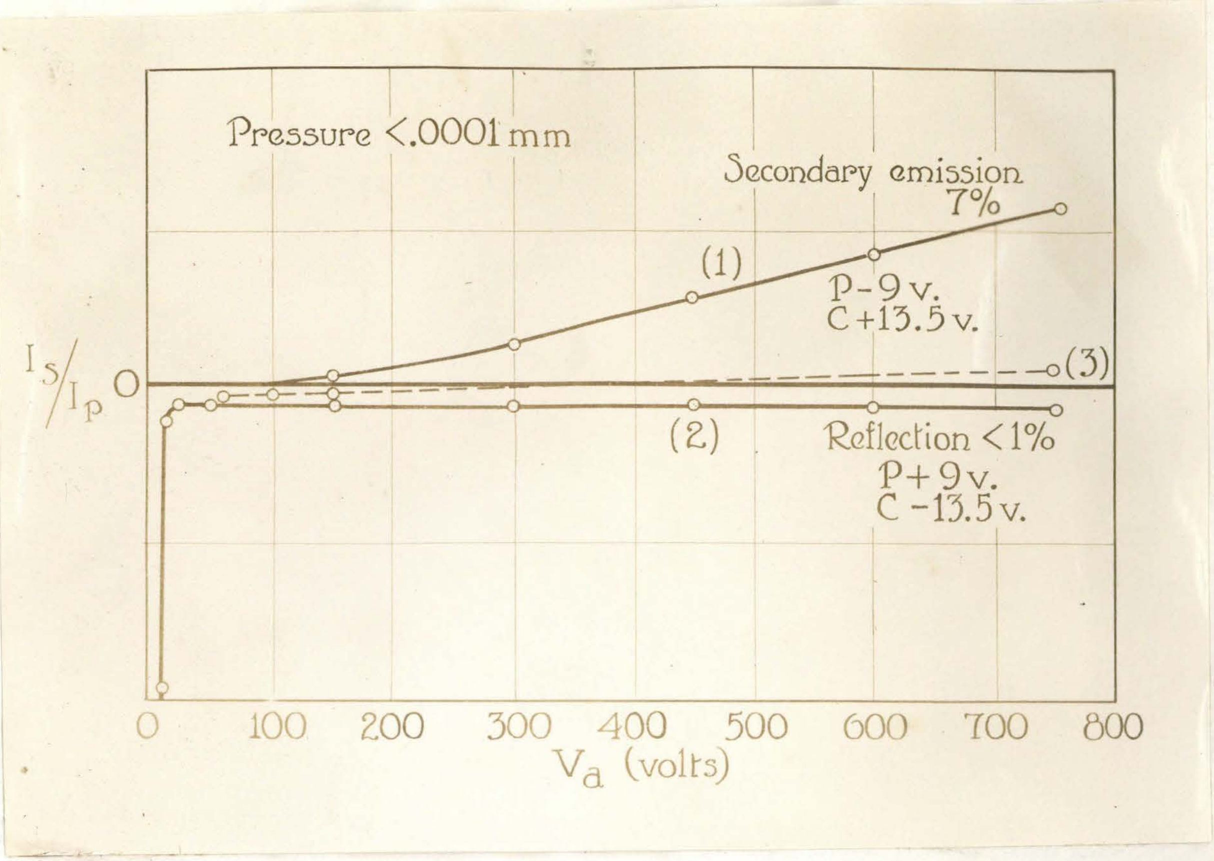


Figure 11. The ratio I_s/I_p as a function of V_a for different arrangements of the collecting potentials at pressure less than .0001 millimeter of mercury, showing effect of secondary emission.

Curve (1) Secondary electrons from grid and plate collected on the collector, S.

Curve (2) Reflected and scattered positive ions collected on the collector, S.

Curve (3) Amount of secondary effect actually observed in runs where V_s V_p, with both potentials positive.

photoelectric effect upon metals is probably dependent upon gas pressure since any radiation with energy sufficient to liberate electrons must come from highly excited gas atoms. Hence this may be a serious impediment to success, as all other secondary effects were assumed to be maximum at low pressure. However, by keeping $V_p = 10$ volts positive, no photoelectrons would be liberated with energy sufficient to escape to the collector. It is conceivable that the photoelectric currents from the plate in the case where V_p was negative (compare Tables I and II, p. 25-26) account for the larger efficiency of ionization in this case. In fact, changing the potential of P should, with sufficient refinement of measurement, serve to distinguish photoelectric effect from ionization and secondary emission phenomena. Third, Brode raises the objection that ionization may be produced by collisions between two metastable atoms and that such collisions might occur with great probability at the high pressures used. No check of this point has yet been devised, and it stands as a valid criticism of interpretation. However, if a positive ion can impart energy sufficient to raise an atom to a metastable state upon collision, it would seem reasonable to expect some impacts to result in complete ionization although, admittedly, the ratio

$$\frac{\text{Energy required to Ionize}}{\text{Energy required to Excite}}$$

is greater for positive ions than for electrons, due to the intense positive field from which the electron must escape in the former case.

It has been questioned by some writers whether positive ions can ionize gas without acquiring the actual <u>velocity</u> obtained by electrons which ionize,--without passing through thousands of volts accelerating potential. A 100 volt K+ ion has the same kinetic energy as a 100 volt electron, but its velocity is that of a 0.00135 volt electron,--*far* below ordinary ionizing potentials. These experiments and those on secondary emission show without a doubt that positive ions of 100 volts and over are able to affect both gases and metals, causing the liberation of electrons from them. This represents some five or ten times the *energy* necessary for electrons to produce similar results, and the efficiency of the ionization is far smaller than for electrons as shown in Table III.

Nothing can be said at the present time regarding the *probability* of an impact between a certain velocity positive ion and a gas atom resulting in ionization, for we do not know yet what the mean free path of these positives is in the gas. We can calculate the efficiency of ionization expressed as the number of ions formed per positive ion per centimeter path at one millimeter pressure without knowing the mean free path of the ions. The abnormally high pressures at which the effect of ionization occurs, roughly ten times the pressure expected on kinetic theory calculations, is striking evidence that the kinetic theory mean free path calculation does not hold for these positive ions. They apparently exhibit a remarkable propensity for getting through the 5 cm path from filament to plate, even against a 10 volt retarding potential in the latter half of their path, without heavy scattering in spite of suffering 50-100 (kinetic theory) collisions. We must conclude that they lose only a small fraction of their forward momentum, on the average, upon an encounter with a gas atom.

This abnormally high mean free path for positive ions has been observed by other workers whose conclusions agree at least qualitatively with the observations of this experiment. Among those who have dealt with this aspect of positive ion kinetics are Dempster10), Kennard26), Durbin27), and Harnwell28). Similar studies for slow electrons (one paper on positive ion mean free paths) have been carried on by Ramsauer29). The first three observers worked with magnetic analysis apparatus which is better suited for analyzing the mean free path than is the one used in these experiments. They give mean free paths up to ten or fifteen times the kinetic theory values for slower positive ions than those used in this experiment.

CONCLUSION.

The success of this experiment in detecting ionization by positive ions where other workers failed may be attributed largely to:

1) Consistent efforts to account for and to eliminate secondary effects.

2) A convenient hot-anode source of positive ions.

3) Extension of observations into higher pressures.

The phenomenon of positive ion ionization has been shown to exist in several gases for K^+ ions above 100 volts, and the efficiency of the effect has been calculated to be less than 4% of that for electron ionization in the gases studied. There still remain for future work the development of greater refinement and variety of methods, the extension of observation to a larger number of gases and to a variety of sources of positive ions; and finally, adequate theoretical interpretation of results.

It is a pleasure to the author to acknowledge his indebtedness to Dr. R. A. Millikan for his interest and helpful discussion of the problem; to Mr. Willy Uyterhoeven and Dr. L. B. Loeb for their constructive criticisms; and to Mr. William Clancy for his assistance in the glass blowing; and to Mr. J. C. Mouzon for his help in the latter part of the experimental work.

Pasadena, California,
May 10, 1929.

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