IONIZATION OF THE NOBLE GASES BY SLOW POSITIVE ALKALI IONS

THESIS

by

James Carlisle Mouzon

In Partial Fulfillment of the Requirements
for the degree of
DOCTOR OF PHILOSOPHY

California Institute of Technology
Pasadena, California
1932

INTRODUCTION

The problem of the ionization of gases by impact of positive ions at low velocities is one in which it is necessary for a large amount of experimental evidence to be gathered before the theorist is able to hazard an intelligent guess at the processes involved. The material herein presented represents the essential advances that have been made in this field.

As is usually the case it is impossible to say when and by whom investigations have begun on a particular problem. So it is with this problem. However, the history of its development up to a few years ago is one of a series of experiments giving either absolutely negative results, or results completely masked by secondary effects. It was because of these past futile attempts to obtain any conclusive evidence that Professor R. A. Millikan suggested to A. L. Klein at the California Institute in 1922 that he take up very carefully first the study of the possible ionization produced when positive ions impinge upon a metal surface. This proved to be a step in the right direction since Klein 1) found for the first time, and this was subsequently checked by other investigators, that positive ions of relatively low energy are quite capable of ejecting electrons from metal surfaces. He found further that the effect began to set in at an energy of the order of 100 volts, and also that positive ions, themselves, may be reflected from surfaces. It was then obvious that an apparatus which would prove successful in detecting pure ionization ia a gas must be so built that it would be able to make these surface effects negligible, or else measurable independently of the main gas phenomenon. Such an apparatus was first built by R. M. Sutton with the advice and assistance of Professor Millikan at this Institute. The design of this apparatus had been suggested by Professor Millikan as early as 1924. A detailed account of it and of the difficulties encountered was given in Sutton's Ph. D. thesis in 1929 and, in a condensed form, in the Physical Review of March, 1929.

The results of Sutton will be summarized briefly thus: Neon and argon were bombarded by singly charged positive ions of potassium of energies up to 750 volts. The collecting potentials were so adjusted as to eliminate practically all secondary effects due to the ions and to enable him to collect any electrons liberated from the gases. A variation of pressure from 0.005 to 0.1 mm gave a definite variation in the ionization. This fact alone was sufficient to prove very definitely that the electrons collected were due to ionization of the gas. This was the first conclusive evidence presented by anyone on this subject. Sutton found that argon was ionized more efficiently than neon when potassium was used as an ionizing agent. Ionization was not observed when the bombarding ion had a velocity of less than about 100 equivalent volts. However, since his galvanometers did not afford high enough sensitivity, he was unable to measure the insetting potential accurately or even to prove that a sharp insetting potential actually exists. It will be well to add that the technique he divised for the collection of the initial positive ions and the electrons arising from the bombarded gas is essentially that which has been used by all observers anywhere who have later taken up and pushed farther the work on the ionization of gases by positives of low energies.

The writer began work with Dr. Sutton in January of 1929. The research was carried on jointly with him until December, 1930. During this period some revisions were made in the apparatus, making the measurements more exact, and the study was carried on in the three noble gases; neon, argon, and helium with the five alkali ions; lithium, sodium, potassium, rubidium, and caesium. The results were published in the Physical Review 2) in April of 1930 and in February of 1931. In December of 1930 the writer continued at the Institute the investigations in krypton and xenon with Dr. Otto Beeck with a much more sensitive apparatus. Dr. Beeck had already studied the ionization in neon and argon by the alkali ions using Sutton's method, but improving the accuracy and sensitivity by separating the alkali ions in a magnetic analyzer and by using sensitive electrometers instead of galvanometers. He published his results in Naturwissenschaften in the summer of 1930 summarizing his work with the statement that the efficiency of ionization in a noble gas is highest for that alkali ion nearest it in atomic number. It will be shown later that this statement is not strictly true. The writer and Beeck also made a very careful study of the potential at which ionization sets in, using the five alkali ions in neon, argon, krypton, and xenon. The ionization in helium is so small that it cannot be studied with any degree of accuracy with this apparatus since the gas pressures are kept low. A summary of these findings appeared in the Physical Review for September, 1931. A more detailed account was given in two articles in the Annalen der Physik, 5. Folge. Bd. 11. 1931 Nr. 6 & 7.

A description of the apparatus used in the work with Sutton and Beeck will be given with the results obtained in each case. It will be of interest to see that, although the apparatus used in the earlier work was not built for exact quantitative measurements, the agreement in the results obtained with the two different apparatus is surprisingly good. Section (1) will treat the work with Sutton while that with Beeck will be treated in Section (2) of this paper.

SECTION (1)

APPARATUS

All of the work done at this Institute between June of 1929 and December of 1929 was with the apparatus to be described. The only marked change made in the apparatus that Sutton had used in his first work was in the tube in which the ionization took place. Fig. 1 shows the tube formerly used by Sutton (3). Fig. 2 shows the experimental tube and the electrical connections employed in the work here presented.

The source of the positive ions was a 0.0005 inch platinum foil 0.3 by 1.2 cm resting in a half cylindrical porcelain trough held rigidly between copper terminals. A thin coat of oxide catalyst, containing a small percent of the particular alkali desired, was spread on the foil. This type of source was originally developed by C. H. Kunsman (4). The oxide was reduced in an atmosphere of hydrogen before it was put into use. The filament was heated by a heavy duty 6 volt storage battery using a current from about 4.5 amperes to 7.5 amperes. As is expected from the work functions of the alkalis, it was observed that the current required for emission decreases with the increase of the atomic weight of the alkali ion. By this method it was possible to obtain singly charged positive alkalis. Several minutes of heating were required before the emission became constant. This preliminary heating was probably a great factor in making the results as consistent as they turned out to be, since it partially purified the source by evaporating the impurities. The fact that these sources were not absolutely pure was obviously one which prevented the results from being of a quantitative nature. Recent study of these sources by means of magnetic analysis shows that some purification is obtained by continued heating. The current of the initial positives used in the experiment was of the order of 10^{-8} amperes.

The entire filament, F, was enclosed by a hollow steel cylindrical cathode, C. This prevented any positives from entering the ionization chamber by any other means than the channel. This channel, 1.5 mm in diameter and 2.5 mm long, was found to be the source of considerable secondary emission. The difficulty was obviated by putting a thin ring in it, cutting down the diameter of the hole so that no electrons ejected from the walls of the channel could escape into the ion chamber. This proved to be a valuable remedy. The channel projected through a hole in the collector, S, so that none of the direct positive beam was able to strike it. In Fig. 2 S is the collector for the electrons liberated from the gas. 2.5 cm above S is the grid, G, which defines the upper limit of the ionization chamber. 2 mm above the grid is the plate, P, on which the initial positive beam is measured.

The chief features in which the tube in Fig. 2 differs from that in Fig. 1 are: 1) a ground glass joint by which the repairs on the filament might be easily effected, 2) a greater space between collector, S, and grid, G, from which the products of ionization were collected; and 3) a flat plate, P, placed only 2 mm above the grid and parallel to it. The ground glass joint consisted of two parts. The upper part was coated with graphite and the lower with stopcock grease, and sealed with mercury. The region between these two parts was pumped out continually, minimizing the danger of grease vapor entering the tube. By placing the grid 2.5 cm above the collector a larger volume was made available in which the ionization might occur. This increased the sensitivity of the measurements. Furthermore, any trouble arising in the old tube (Fig. 1) by ionization above the grid was done away with by making the plate, P, flat and placing it only 2 mm above the grid. It was found that the reflection of the positives from P was of no consequence, so that the V-shaped plate previously used to reduce the reflection was eliminated. As a matter of fact, a small reflection of positives from the plate was sometimes recorded when no gas was present in the tube, but this seemed to reach its maximum value at about 80 volts and decrease when the voltage was increased beyond this point.

The electrical connections were as indicated in Fig. 2. A is an ammeter which indicated the filament current controlled by the rheostat in series with the six volt storage battery and the filament. It will be noted that the cathode, C, was grounded through a galvanometer, M. Ions were accelerated from the filament through the channel by means of the battery, Va, which consisted of several banks of small capacity storage cells. V is a voltmeter to record the accelerating potential of the ions.

The galvanometer, M, was not essential to the apparatus. Because of criticism, suggesting that all of the electrons collected on S could have been accounted for by assuming a dark discharge to have taken place between the filament and the cathode, M was placed in the circuit. Any discharge would have caused a sudden jump in the current to the cathode through the galvanometer, M, at some critical point as the filament current, the accelerating potential, or the gas pressure was increased. This criticism proved to be completely fallacious since the current recorded by M never showed any sudden fluctuations under the conditions stated.

The collecting potentials in this type of work are quite critical. A thorough study of these was made by Sutton, so it is only necessary to state what conclusions were reached. The initial positive ions are collected by the plate, P. Now it is desirable to prevent any emission of secondary electrons from this plate. This is accomplished by applying a small positive potential to P, not sufficient to retard seriously the initial beam. Experiments 1) have shown that the velocity of the secondary electrons is rarely over 8 volts. Thus, a potential of 9.5 volts was sufficient to stop all such electrons from escaping the plate. The galvanometer, G_1, which recorded the initial positive ions, is shown connected in series with the 9.5 volt battery, Vp.

The region between the grid and the collector, S, formed the volume from which the products of ionization were collected. The grid was connected to ground, shielding the space below it from the positive collecting potential of the upper plate. The electron collector, S, which served to capture the electrons liberated from the gas, was connected through the battery, V_s, and the galvanometer, G_2, to ground. To be satisfactory, the potential on S must be positive and high enough to give a saturation current of the electrons freed above it. Yet, it must be below the ionization potential of the gas used. Otherwise, the electrons accelerated to S by the collecting potential would have sufficient energy to ionize. In most of the work done with this apparatus 13.5 volts proved satisfactory for this purpose. This method of adjusting the collecting potentials is the same as was used in the investigations that followed; namely, those of Beeck in Danzig 5), and those of Beeck and the writer at the California Institute 6).

The galvanometers, G_1 and G_2, had sensitivities of the order of 10^{-9} amperes per millimeter deflection on a scale placed at a distance of 3 meters. G_2 was about twice as sensitive as G_1 in the work done on helium. In all of the rest of the work G_2 was about seven times as sensitive. The ratio of the sensitivities was checked at frequent intervals by applying a known current derived from a bridge across a battery and sent through the galvanometers in series with 500000 ohms.

The apparatus was evacuated by means of two stages of mercury diffusion pumps backed by an oil pump. Gas pressure was measured by a McLeod gauge. Liquid air was used to freeze out any water, grease, or mercury vapor that might have been present. The neon and argon used were pure to less than a half of one percent. However, they were passed through a magnesium discharge tube to make certain that they were not contaminated. Much difficulty was encountered at first with the purity of the helium used. It was obtained from the United States Bureau of Mines at Amarillo, Texas in a moderately pure form. By passing it over oxidized copper turnings and charcoal in liquid air, and then through the magnesium discharge tube, it was made spectroscopically pure. Consistent results were obtainable after this process of purification. Since the efficiency of ionization in helium is very small, a slight impurity produces an unusually large effect. After each run, no matter what gas was used, the tube was pumped out and fresh gas admitted before another run was taken. The method used by Beeck and the writer of letting the gas flow steadily through the apparatus is a more convenient way of making certain that the gas is kept pure in the apparatus.

PROCEEDURE

The following proceedure is that used in a typical run. With no gas present the two galvanometer deflections were read when the filament was turned on and an accelerating potential was applied. This gave a measurement of the secondary emission. (Slight variations in filament emission caused no difficulty since corresponding variations in the electron current to the collector plate took place. The ratio of these two currents was taken as a measure of the secondary emission, as well as a measure of the ionization in the gas). After the determination of the secondary emission from the metal parts, the gas was admitted to the tube and time was allowed for the pressure to become constant before the actual run was taken.

During the run the accelerating potential was varied from 100 to 750 volts. Readings of the two galvanometers were taken for each accelerating potential. At the conclusion of the run, just before the gas was pumped out, the positive ion current, I_p, to the plate was read. Call this reading, I_p'. Immediately after this reading was taken the tube was evacuated and G_1 again read. Call this reading, I_{p_0}. These last two readings were taken to correct for the scattering of the initial positives in the gas, as will be explained below. This proceedure constituted a "run".

The efficiency of ionization of a gas by positive impact will be defined as the number of electrons liberated from the gas per initial positive ion per centimeter path per millimeter pressure of mecury at 20 deg. Centigrade. A slight difference in the efficiency is to be found in the definition given in Section (2) since it is there reduced to 0 degrees C. To obtain the efficiency of ionization, N, from the data it is merely necessary to divide the actual electron current, I_s, by the corresponding positive ion current, I_p; then divide the result by the pressure, P, multiplied by the distance from the cathode to the grid. The equation for the efficiency is then:

$$N = \frac{I_s}{I_p \times P \times l}$$

where P is the pressure of the gas in mm of Hg.
and l is 2.5 cm.

I_s is the electron current to the collector.

I_p is the initial positive ion current to the plate.

I_s and I_p must be reduced to the same terms by multiplying by the ratio of the sensitivities of the galvanometers. Let K equal the ratio of the sensitivity of G_1 to G_2. Besides taking care of the ratio of the sensitivities of the galvanometers, there are two corrections that can be applied which will give a more quantitative result. One is that for the secondary emission, which was generally very small. The other is for the scattering of the initial positive beam by the gas. If the latter correction is made, it is seen that, at low gas pressures, the ionization is a linear function of the pressure. At higher pressures multiple collisions take place, spoiling this simple relationship. Making the correction for secondary emission and scattering the equation for the efficiency, N, becomes:

$$N = \frac{I_s' - I_{s_0}}{\frac{I_{p_0}}{I_{p'}} I_{p_1} \times P \times 2.5} \times K$$

where I_s' is the observed electron current to S with gas
present.

I_{s_0} is the observed electron current to S with no
gas present at the same accel. pot. as above.

K is the ratio of the sensitivity of G_1 to G_2.

I_p' is the initial positive ion current to P just
before the gas is removed.

I_{p_0} is the initial positive ion current to P just after the gas is removed.

I_{p_1} is the initial positive ion current to P observed at any time during the run.

Strictly speaking, one could correct for the increase of the positive ion current to P due to secondary electrons leaving it. However, this is absolutely negligible.

A number of measurements with a galvanometer were made to test for secondary emission due to electrons ejected from the grid. This gave a practically negative result.

In order to obtain higher sensitivity the gas pressure was often increased above the point where the mean free path was of the order of the distance from the collector to the grid. This gave rise to multiple collisions of the positives on their way to the upper plate, thus causing more electrons to be liberated from the gas. This procedure was particularly helpful in getting a qualitative idea of the ionization in helium. Ionization was not detectable at pressures as low as 0.005 mm where the kinetic mean free path is comparable with the dimensions of the apparatus.

Fig. 3 shows the ratio of I_s/I_p plotted against the accelerating potential for different pressures. These curves were then reduced to one curve for N, the efficiency, plotted against the accelerating potential as is shown in Fig. 3a. (N for argon and neon are those obtained by Sutton previously. [3)]) To obtain N for helium, the ratio of I_s/I_p was divided by the average pressure multiplied by the path length. The increase with pressure was expected in the value of N since multiple collisions took place with the high pressures used in helium. Therefore, the quantitative value of N in helium is not to be taken too seriously. The correction for the scattering of the initial beam was not applied in the case of helium. The fact that the curves in Fig. 3 taken at pressures of more than 0.05 mm seem to be shifted bodily upward is undoubtedly due to this scattering.

RESULTS

Figures 5 and 6 show the efficiency of ionization, N, plotted against the accelerating potential of the various alkali ions in neon and argon. Fig. 5 shows the ionization in neon beginning in the neighborhood of 150 volts and increasing linearly with the accelerating potential to 750 volts, the highest value used. The slopes of the curves in both figures suggest a non-asymptotic approach to the axis. No quantitative conclusions can be drawn from these curves as far as the insetting potential is concerned, since the positive ion source most certainly consisted of a mixture of two or more alkalis. Magnetic analysis indicates that sodium is present in nearly all of the catalysts. One can explain the fact that Fig. 5 shows all of the positive ions beginning to ionize at about the same potential by saying that sodium was present in all of the sources of ions. Since it is seen that sodium ionizes neon most efficiently, it follows that any sodium impurity would make the insetting potential for any other ion the same as it is for sodium. Naturally, the most efficient ionizer produces ionization at the lowest potential.

Two important facts are to be drawn from the curves in Fig. 5 and Fig. 6. These are:

1. Sodium is the most efficient ionizer in neon, while potassium is most efficient in argon.

2. The slopes of the curves near the axis indicate that there may be a sharp insetting potential of ionization. On this evidence alone one can not come to that conclusion, since the method is not sensitive enough. It does, however, hint strongly at the result obtained later.

In Figures 6 and 7 N is plotted against the atomic weight of the ionizing agent. By plotting N against the atomic number, which is the same as plotting it against the atomic weight, Beeck 5) reached the conclusion that the ionization of a noble gas is best effected by that alkali ion closest to it in atomic number. The experimental work done by Beeck and that presented here indicated that this was true. This conclusion was based on the data obtained from helium, neon, and argon. In the next section it will be shown that this conclusion is not strictly valid. It is fitting to summarize other results of this present research as was done by Sutton and the writer in the Physical Review, vol. 37, Feb. 15, 1931.

Similar results have been published recently by Dr. Otto Beeck[15] who secured homogeneous beams of positive ions by means of a magnetic analyzer. His method is evidently better designed for the purpose than the one here reported, and he is now in a position to complete the study of the two remaining noble gases at this Institute. The qualitative agreement between the two methods is excellent, and the quantitative agreement is as good as might be expected considering the difference in methods. The only marked departure from regularity of our results appears in the relative interchange of intensities of ionization by lithium and sodium in argon. This may be accounted for by either or both of two causes: first, an impurity of higher atomic weight in the lithium source derived from powdered spodumene (all other sources were Kunsman catalysts); second, the unaccountably large reflection of sodium ions by argon. This inversion of position was carefully checked, and as far as the accuracy of this method is concerned, the effect is real.

Not only is there maximum ionization produced by the alkali positive lying closest to the atomic weight of the gas bombarded, but the intensity of these maxima increases greatly in the heavier gases. The ionization of helium is very feeble, whereas in argon it is quite pronounced. It is rather to be expected that even greater ionization will be found in xenon and krypton. In all of the foregoing work, correction has been made for the secondary emission of electrons from the metal parts of the tube. Inasmuch as there was gas admitted into the tube, no particular precautions were taken to outgas the electrodes. Comparing the secondary emission of the metal surfaces under bombardment of the various alkali ions, the intensity of emission was found to vary in the same way as the intensity of ionization; i.e., greatest for potassium when argon had been present, etc. It would appear that the secondary emission might be due largely to a layer of gas upon the electrodes, and hence this surface effect would bear a close relationship to the volume ionization produced in the gas by different positive ions.

In concluding the discussion of the work of Sutton and the writer it will be worthwhile to say a few words concerning the essential improvements necessary to make the apparatus of more use quantitatively. The purity of the positive ions was obviously one thing that had to be made more certain. The sensitivity of the measurements was seriously hampered, since the galvanometers used had not, at their best, a sensitivity better than 10^{-10} amp. per mm deflection on the scale. An ionization chamber with metal walls is far more to be desired than one with glass walls which are likely to be charged electrostatically. This, then, is another criticism that can be made of the apparatus. However, since the data could be reproduced from time to time, this point is not too serious.

A further difficulty with the measurements, which has never been fully corrected in any of the apparatus built, was the scattering of the initial positive ion beam by the gas. A method for determining the quantity of scattering was used, and was discussed previously. (see page 12). Recent work with accelerating potentials up to 2000 volts indicates that this scattering is of a more serious nature at higher voltages. Mention was made on page 16 of an unaccountable reflection of sodium in argon. Later works seem to confirm this, though this reflection is not so pronounced if the gas pressure used is small, and causes no trouble at velocities below 500 volts.

SECTION (2)

This section of the paper describes the apparatus designed and used by Beeck in Danzig. One can see that it obviates the two essential objections to the more simple arrangement described in the previous section. The apparatus was brought to the California Institute by Dr. Beeck in 1930, and the work was continued jointly with the writer.

Figure 8 shows a cross section of the ionization chamber and magnetic analyzer. The ions are accelerated from the filament to slit # 1 by means of a small potential of the order of six volts, applied at the center of a high resistance across the filament. The ions enter the magnetic field, M, at the first slit, and are deflected through 90 degrees. Their circular path is defined by the three slits indicated. A second variable accelerating potential is applied between slits 3 and 4, giving the ions any energy desired. Slits 2X6 mm proved sufficient to give good resolution of the alkalis. A constant potential was maintained between the filament and the first slit. The different alkali ions were brought onto the third slit by varying the magnetic field.

The ionization chamber is seen to be essentially the same as that shown in Fig. 2; the only difference being in the collector, I, for the initial beam. Beeck constructed it in the form of a cage of four concentric cylinders of brass. The walls were coated with soot from a flame of natural gas bubbled through benzene. This was done to prevent the reflection of the initial positive ion stream. One might criticize this construction because of the possibility of ionization occurring above the grid, causing the electrons resulting therefrom to be collected on I, decreasing the positive current. (The plate, P, in Fig. 2 was made flat to assure that this did not happen). However, in the present case, it is pretty certain that the electric field from the grid does not penetrate far enough into the cylinders to cause any disturbance. Any ions formed inside the cage simply recombine or go to the walls, making the total addition in charge zero.

The rest of the chamber is identical to that in Fig. 2. The channel is seen projecting through the collector. At its lower end is a thin ring to prevent any electrons from being ejected from the walls of the channel by the positives. The whole ionization chamber was enclosed in a soft iron cylinder 5 mm thick to shield it from any stray magnetic field from M. It was maintained at ground potential with the grid connected to it. The iron cylinder served as the wall of the ionization chamber.

Fig. 9 shows a diagram of the apparatus with the electrical connections. The positive ions and the electrons were recorded by means of the electrometers, E_1 and E_2, respectively. These electrometers were of the single string type. It can be seen by comparing Fig. 9 with Fig. 2 that the electrical connections are very much the same as far as the ionization chamber, itself, is concerned. E_1 and E_2 are shown with their plates maintained at a constant difference of potential by means of auxiliary batteries. The center tap of each of the batteries is connected to the case of the corresponding electrometer. This center tap also fixes the potential of the shield and the lead to the collector plate. The string is permanently connected to the collector plate and is connected to the center tap of the battery through the grounding switch, H. When a run is taken this grounding switch is opened, allowing the charge to be registered by the deflection of the string.

The initial accelerating potential of six volts that is applied between the filament and the first slit was chosen small in order that the magnetic field could be small. This eliminated strong stray fields in the neighborhood of the ion chamber. It so happens that this choice was a wise one from another standpoint. The Maxwellian distribution of velocities of the ions emitted from a hot source can cause considerable uncertainty, but if the distribution is over only six volts out of a hundred or more, the error is very small. Thus applying nearly all of the acceleration between slits 3 and 4 after the ions have been emitted, one automatically gets ions of very uniform velocity.

The fact that the electrometers allow from 10000 to 100000 times the sensitivity of the galvanometers used in the previous work makes it possible to work with smaller pressures. In the work here presented the gas pressure used was never in excess of 0.007 mm of Hg. The mean free path at this pressure is something like 2 cm, while the path length of the apparatus is 2.8 cm, so that multiple ionization by a single ion is excluded.

It is seen that the two worst faults of the early apparatus have been eliminated. One is now sure of his ions being of but one alkali, and one has measuring devices sufficiently sensitive to warrent his obtaining quantitative results. But, as a matter of interest and information, let us look at Fig. 10. Here is a comparison made by Beeck of the results he obtained for potassium ions in argon and neon with those first obtained by Sutton with his original apparatus. The agreement of the curves in argon is much better than one would expect under the circumstances. The more steep ascent of the curve in neon obtained by Sutton can be accounted for, in the light of our present knowledge, by the presence of sodium ions in the potassium source. Sodium ionizes neon more efficiently than does potassium, and therefore a mixture of the two ions is more efficient than potassium, alone.

The string electrometers used in this work were built by the instrument shop of the California Institute. A particularly noteworthy feature in these instruments is that the objectives in the microscopes hav~~ing~~e a working distance of 19 mm. This allows a great deal of freedom in adjustment. The objectives were 12 power, while the oculars were 25 power. The strings were made of 0.003 mm. Platinum wires obtained from Wollaston wire. It was found very convenient to project the strings onto a transparent scale, This facilitated the reading of both instruments simultaneously by one observer. The scale was placed at a distance of about six inches from the eyepieces. A very distinct image was obtainable. All readings were estimated to a tenth of a millimeter.

The leads of the electrometers were carefully insulated with amber. Those leading into the vacuum were sealed with picein ~~was~~ which was cautiously melted to avoid carbonizing it, since the insulating qualities are spoiled if it is the least bit burned. There were no electrical leaks large enough to interfere with the readings. The time of charging up the electrometers was never over twenty seconds, even when making the exact measurements of the insetting potentials. The leads were shielded by means of 5/8 inch brass tubing. Special care was taken that all shields of the same electrometer system were at the same potential by soldering a continuous wire to all parts.

Contact in the grounding switches, shown as H, was made between phosphorus bronze and brass. It was necessary to clean these surfaces from time to time. Platinum contacts are more advisable. The switches were operated by means of small electromagnets. These proved much more satisfactory than the usual strings.

The voltage sensitivity of the electrometers was measured by applying a known potential by means of two dial resistance boxes hooked up as a potentiometer. This was checked several times during runs, a calibration curve being plotted for the variation of deflection with applied potential. A small switch, not shown in Fig. 9, was used to connect the two electrometer systems together to measure their relative capacities.

Since one wants only the ratio of the charges collected on the two plates and recorded by E_1 and E_2, it is not necessary to know the actual capacities of the electrometer systems. It is sufficient to know just their relative capacities. To do this a charge is placed on E_2 raising it to a potential, V_2. By connecting the system of electrometer, E_2, to that of E_1 the potential falls to a value, V_1. The ratio of the capacity of E_1 and its leads to that of E_2 and its leads is given by the equation:

$$\frac{C_i}{C_e} = \frac{V_1}{V_2 - V_1}$$

This ratio was found to be 1.73. It is necessary that this ratio be measured with the instruments adjusted to the sensitivity used in the runs. Also it must be measured with the deflection of E_2 about the same as that used in the runs. This precaution is necessary since the effective capacity of the system is a function of the sensitivity as well as the deflection.

The apparatus was evacuated by means of a fast mercury diffusion pump backed by a double stage diffusion pump and an oil pump. The first pump evacuated the region between slits 3 and 4 and that between the pole pieces of the magnet. (see Fig. 8). The gas was admitted to the ionization chamber above the fourth slit by means of a fine capillary tube. It was pumped continuously through the chamber and out of slit 4. Fast pumping was necessary to prevent the pressure below the fourth slit from rising so high that the ions would suffer collision on their way from the filament to the ionization chamber. With the arrangement used it was possible to work with pressures in the ionization chamber up to 0.008 mm. A McLeod gauge was connected to the ionization chamber to record the pressure.

The gases used were better than 99.5% pure. No further attempt at purification was made. Liquid air was used to freeze out vapors. To get the gas to the ionization chamber it was first allowed to enter a reservoir until the pressure there was about 6 cm as recorded by a manometer. The stopcock between the gas container and the resevoir was then closed. The gas from the reservoir was admitted by means of a stopcock through a capillary tube to the ionization chamber. With the pressure of 6 cm in the reservoir the pressure in the ionization chamber was maintained at about 0.005 mm. Naturally this pressure decreased slowly with time. The pressure was measured at frequent intervals while runs were being made, and was plotted as a function of the time. It was easy to determine the pressure very accurately at the time any particular reading of the electrometers was made by referring to this pressure-time graph. The rate of decrease of pressure was usually about 0.00005 mm per minute.

The following procedure is that used in a typical run. With no gas present the filament is turned on, the magnetic field of the mass spectrometer being such that the desired alkali ion reaches the ionization chamber. The two grounding switches of the electrometers are then opened simultaneously. As soon as a sufficient charge has collected on E_1 the filament current is turned off, and the deflections on E_1 and E_2 are observed. This first measurement is for secondary emission from the metal parts. In none of the work presented here was there any recorded. The gas is now allowed to flow through the apparatus and time is allowed until equilibrium is reached. A run is then made recording the deflections of the electrometers corresponding to given accelerating potentials. The time at which each reading is taken is noted so that the pressure of the gas can be determined from the pressure-time graph. By finding the potentials on the strings of the electrometers corresponding to the deflections from the voltage sensitivity curves one has all of the data necessary to make the calculations.

To find the number of electrons liberated from the gas per initial positive ion per cm path per mm pressure at zero degrees centigrade the following formula is used:

$$N = \frac{Q_e}{Q_i \times l \times P \times {}^{273}/_{293}}$$

where Q_e is the charge of the electrons liberated.

Q_i is the charge of the initial positives.

l is the path length in the apparatus and is 2.8 cm.

P is the pressure at room temperature.

To get N in terms of the data collected one writes $Q_e = C_e V_e$ and $Q_i = C_i V_i$, where C_e is the capacity of E_2 with its leads and C_i is the capacity of E_1 with its leads. V_e and V_i are the potentials corresponding to Q_2 and Q_1, respectively.

Then, $$\frac{Q_e}{Q_i} = \frac{C_e V_e}{C_i V_i} = \frac{V_e}{V_i \times {}^{C_i}/_{C_e}}$$

Now C_i/C_e was measured and is 1.73, and V_e and V_i are taken from the voltage-deflection graph, and P is found on the pressure-time graph. So we write the efficiency of ionization as:

$$N = \frac{V_e \times 293}{V_i \times P \times 1.73 \times 2.8 \times 273} = 0{,}222 \frac{V_e}{V_i \times P}$$

In the investigation of the efficiency of ionization of gases by the alkalis the sensitivity of electrometer, E_1, was about 60 divisions per volt. (The capacity of it and its leads was about 25 cm) The sensitivity of E_2 was something like 200 divisions per volt. In the study of the insetting potentials the sensitivity of E_1 was kept about the same, while that of E_2 was increased as much as possible. (These electrometers become unstable at about 1000 divisions per volt). In the determination of the insetting potentials the ratio of the deflections alone was plotted. All of the results were reduced to the same terms by reducing them to values corresponding to a deflection of 20 cm of E_1. This was simply the arbitrary standard chosen.

RESULTS

Figures 11 and 12 show the results of the investigations of the efficiency of ionization by the positive alkali ions in krypton and xenon. It will be remembered that the results in neon, argon, and helium Fig. 6) indicated that the alkali closest to the noble gas in the periodic table was most efficient as an ionizing agent of that gas. This statement was first made by Beeck [5).

The investigation of the efficiency of tha alkalis in krypton and xenon was carried out principally to test this maximum effect. One sees from the curves that potassium begins to ionize krypton at a lower potential than does rubidium and is more efficient up to about 400 volts. This point was checked very carefully and seems to be real. Therefore, the maximum effect of ionization by the alkali ion nearest the noble gas in the periodic table is not strictly true.

Figure 12 shows that caesium positives are most efficient in ionizing xenon. It will, however, be noted that potassium positives are more efficient in xenon than those of rubidium. This again indicates that the simple relation of the position of the ionizing agent in the periodic system to that of the ionized gas is not valid. Otherwise, one would expect rubidium to ionize xenon better than does potassium. Thus the collision phenomena are not as simple as the experiments at first might indicate. Undoubtedly, the electron configuration must play a subtle role in these processes. Fig. 13 shows the efficiency of ionization plotted against the atomic number of the positive ion. The curves in neon and argon are those obtained earlier by Beeck. The accelerating potential of the ions at which this data was taken was 500volts. It is a little misleading to look at Fig. 13 without looking at Fig. 11 also, since it alone shows rubidium more efficient as an ionizing agent of krypton than is potassium. This, as is seen in Fig. 11 is true only above about 400 volts.

another interesting conclusion, which was suggested on page 16, is that the maximum efficiency of ionization for a given accelerating potential increases with the atomic weight (or atomic number) of the gas. For example, the efficiency(the number of electrons liberated from a gas per initial positive ion per cm path per mm pressure) of caesium in xenon at 500 volts is 7.2 while that of potassium in argon is 3.4.

Since the experimental work previous to this had given the suggestion that there might be a definite potential at which ionization by positives sets in, special pains were taken to study this point. The data was taken with the electrometers so adjusted that it was possible to measure a charge on the electron collector plate of the order of one five thousandth of that on the positive ion collector plate. As the accelerating potential was increased from zero the ionization remained zero up to a certain critical point. Above this point the ionization increased almost linearly, showing no indication that it started from zero asymptotically at the lower voltages. This evidence is really new, since the earlier work was not sensitive enough to make this point clear. This definite insetting potential is contrary to the early theories on the subject, such as that of Franck 7). In all cases except that of potassium in krypton it was definitely shown that the ion nearest the noble gas in the periodic system begins to ionize at the lowest potential. Figures 14, 15, 16, and 17 give the curves taken for the insetting potentials of the alkali ions in neon, argon, krypton, and xenon, respectively. The table in Figure 16 shows the values of these potentials. The question marks indicate uncertainties of about 10 volts in the values given. One should observe the fact that the insetting potential of potassium is next to that of sodium in neon, lowest in argon and krypton, and next to caesium in xenon.

The efficiency of ionization by positive ions is of the same order of magnitude as that by electrons when the energy is above about 400 volts. Electrons have reached their maximum efficiency by that voltage and their efficiency is either constant or drops off slightly thereafter. The maximum efficiency of electrons is considerably greater than that by positives of the same energy. K. T. Compton and van Voorhis 8) give the maximum efficiencies for electrons as 3.2 in neon, 10.33 in argon, and 9.96 in nitrogen. The accelerating potentials of the electrons corresponding to these maximum efficiencies are: 340 volts in neon, 140 volts in argon, and 175 volts in nitrogen. The efficiencies of positives at these corresponding energies are: 0.6 for sodium in neon, and 0.6 for potassium in argon. No value can be given for positives at 175 volts in nitrogen. However, the efficiencies of positives at 500 volts are more than that of electrons at the same energy in neon and argon. That can also be said of nitrogen since it and air too were investigated by Sutton and the writer. As yet the maximum efficiencies have not been determined for the case of the positive alkalis in the noble gases.

A most interesting result is obtained if the probabilities of ionization are computed for the most efficient alkalis in their neighboring gases. The probability of ionization is simply the chance that an electron will be liberated when the positive ion collides with a gas atom. It is obtained by dividing N, the number of electrons liberated per initial positive per cm path per mm pressure by the number of collisions the ion makes per centimeter. The probability, P, is then, $P = NL$, where L is the kinetic theory mean free path at 1 mm pressure. The kinetic theory mean free path is not quite the correct value to use, but it is certainly of the right order and is as good as any other value we know, unless the collision cross-section values 9) are a trifle better. The table below gives the values of the probability of ionization thus computed.

	P
Na^+ in neon------	0.025
K^+ in argon-----	0.026
Rb^+ in krypton---	0.038
Cs^+ in xenon-----	0.030

These values are for an accelerating potential of 500 volts. Because of the general shape of the curves of the efficiency of ionization plotted against accelerating potential, these values will remain the same for potentials of more than about 200 volts. It is interesting that these probabilities come out almost equal. As a matter of fact, bombarding a gas the electron has to escape the field of the oncoming ion plus that of the positive charge left on the atom from which the electron is ejected. Likewise, doubly ionized calcium, for example, should ionize argon much less efficiently than does singly charged potassium, though the masses are about the same. The case of the bombardment of argon by neutral argon atoms was recently studied successfully by Dr. Beeck 11) and the conclusion reached agreed with Zwicky's prediction. It would be of interest to investigate the ionization of the noble gases by doubly charged alkali earths if a suitable source could be developed. The field of study of atom beams received an impetus by the work of Kallman and Rosen 12) in 1930. Much fruitful material should be derived from this kind of work.

It is worthwhile to know if there is a maximum efficiency of ionization by positives, and at what potential this maximum occurs. The curves already presented indicate that such a maximum exists, as one would expect. An early attempt to use higher accelerating potentials was made by Sutton and the writer, but the apparatus was not suited for velocities over 900 volts. No maximum was observed up to that point. A new apparatus has been constructed by the writer to study this and allied questions. A good deal of difficulty has been encountered by the reflection of the high velocity ions.

In conclusion the author wishes to express his gratitude to Dr. R. A. Millikan for his interest and for his helpful discussion of the problem; to Drs. R. M. Sutton and Otto Beeck for their advice and cooperation in the experimental work; and to Dr. Fritz Zwicky for his interest in the theoretical expla~~i~~nation of the phenomena observed.

SUMMARY OF RESULTS

The study of the ionization of the noble gases by slow positive ions presented herein leads to the following conclusions:

1. The relative masses of the ion and gas atom play an important role in the process of ionization. This is concluded from the fact that the most efficient ionizing agents in helium, neon, argon, and xenon are: lithium, sodium, potassium, and caesium, respectively. In these cases mentioned ionization is best effected in a noble gas by that alkali ion nearest the noble gas in the periodic system. This is not true in the case of krypton, where potassium ionizes better than does rubidium up to an accelerating potential of 400 volts. Other evidence is presented which indicates that the phenomenon of ionization by slow positives is not entirely due to a simple "mass effect".
2. The maximum efficiency of ionization for a given accelerating potential increases with the atomic number of the gas.
3. A definite threshold potential exists at which ionization begins. This is contrary to expectations based upon previous theory.
4. The efficiency of ionization (the number of electrons liberated from the gas per initial positive per cm path per mm pressure) by positives is of the same order of magnitude as that by electrons when the energy is above

about 400 volts. The maximum efficiency of ionization by electrons is considerably greater than that by positives of the same energy. The maximum efficiency of ionization by positives has not been determined, but may well be much greater than that by electrons.

5. The probability of ionization (the chance of an electron being liberated from a gas atom when a positive ion strikes it) by a positive alkali ion in the gas closest to it in the periodic system is approximately the same, regardless of the alkali. Kinetic theory mean free path is used in this computation.

6. Secondary emission of electrons from metal surfaces by positive ion bombardment is the same function of the adsorbed noble gas as the ionization of the gas itself.

7. The heating current of the source of positive ions necessary to produce emission, when a given accelerating potential is applied, increases as the atomic weight of the alkali ion emitted decreases.

REFERENCES

1) Klein- Phys. Rev. 26. 800, 1925.

2) Sutton & Mouzon- Phys. Rev. 35, 694, 1930.

2) Sutton & Mouzon - Phys. Rev. 37, 319, 1931.

3) Sutton- Phys. Rev. 33, 364, 1929.

4) Barton, Harnwell, & Kunsman- Phys. Rev. 32, 629, 1928.

5) Beeck- Ann. der Phys. 6, 1001, 1930.

6) Beeck & Mouzon- Phys. Rev. 38, 967, 1931.

6) Beeck & Mouzon- Ann. der Phys. 11, 737 and 858, 1931.

7) J. Franck- Zeits. f. Phys. 25, 312, 1924.

8) K. T. Compton & van Voorhis- Phys. Rev. 26, 1925.

9) Ramsauer & Beeck- Ann. der Phys. 87, 1, 1928.

10) Zwicky- Proc. Nat. Academy of Sc. 18, 314, 1932.

11) Beeck- Proc. Nat. Academy of Sc. 18, 311, 1932.

12) Kallmann & Rosen- Zeits. F. Phys. 61, 61, 1930.

12) Kallmann & Rosen- Zeits. F. Phys. 64, 806, 1930.

ILLUSTRATIONS

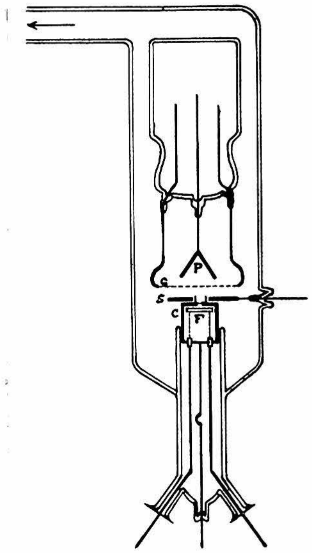

Fig. 1. Positive ion ionization tube.

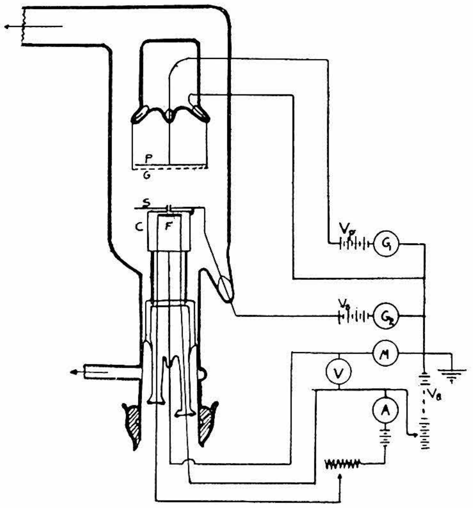

Fig. 2 Experimental tube and connections.

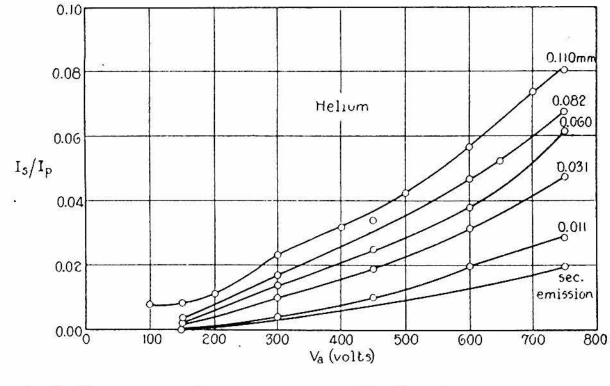

Fig. 3 Ionization in helium at various pressures. Ratio of electron current to collector to positive ion current to plate as function of accelerating potential of positive ions.

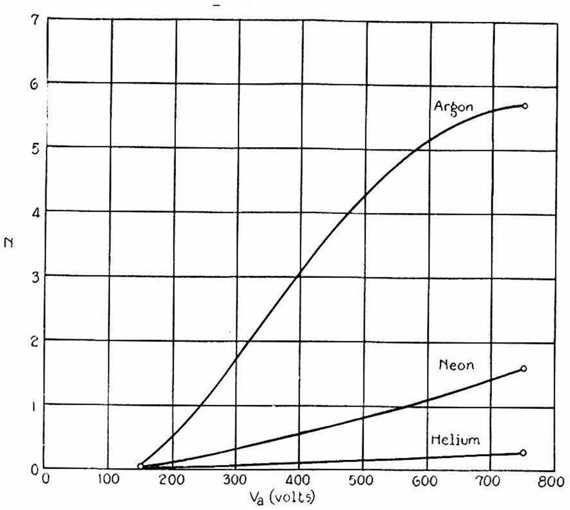

Fig. 3a Comparative ionization of argon, neon, and helium by potassium positive ions. *N* represents the number of ions formed per positive ion per cm path at 1 mm pressure.

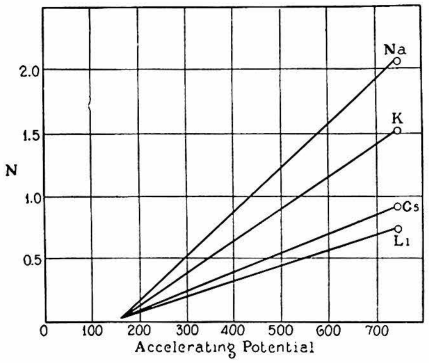

Fig. 4 *N*, number of neon ions formed per initial positive ion per cm path at 1 mm pressure.

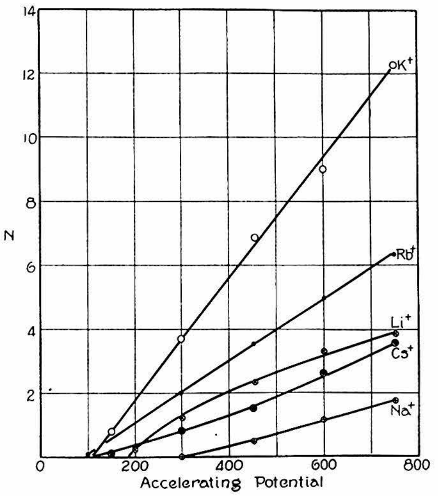

Fig. 5 *N* for argon.

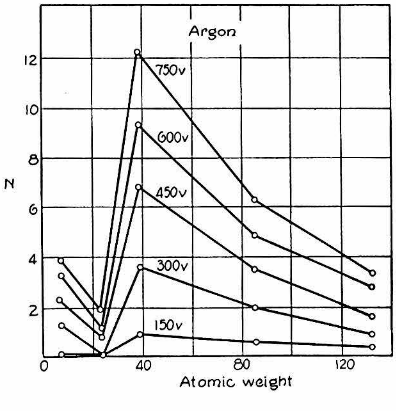

Fig. 6 *N* as function of atomic weight of positive ions and their energies.

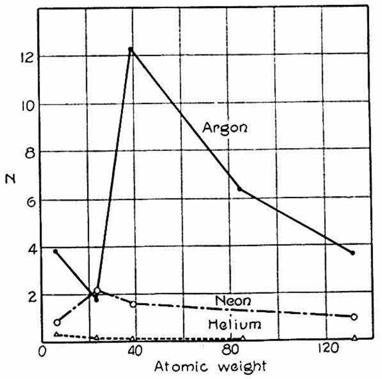

Fig. 7 Comparative values of ionization at 750 volts accelerating potential for different gases as function of atomic weight of ionizing agent.

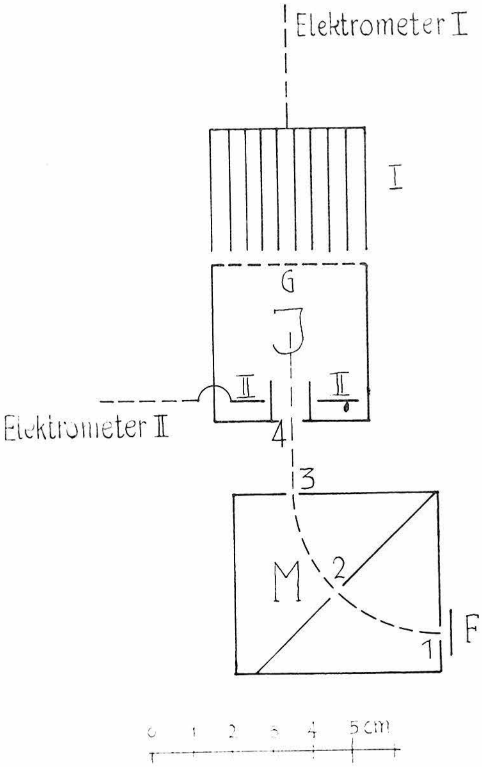

Fig.(8) Ion Chamber and Magnetic Analyzer

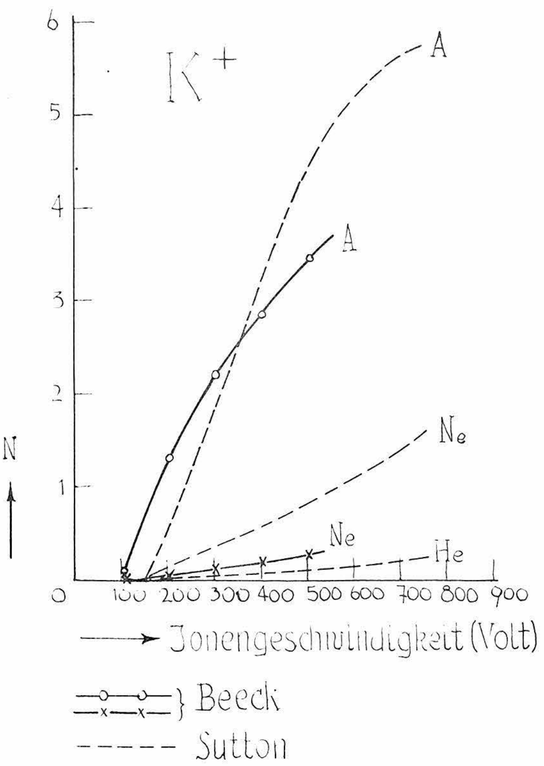

Fig.(10)

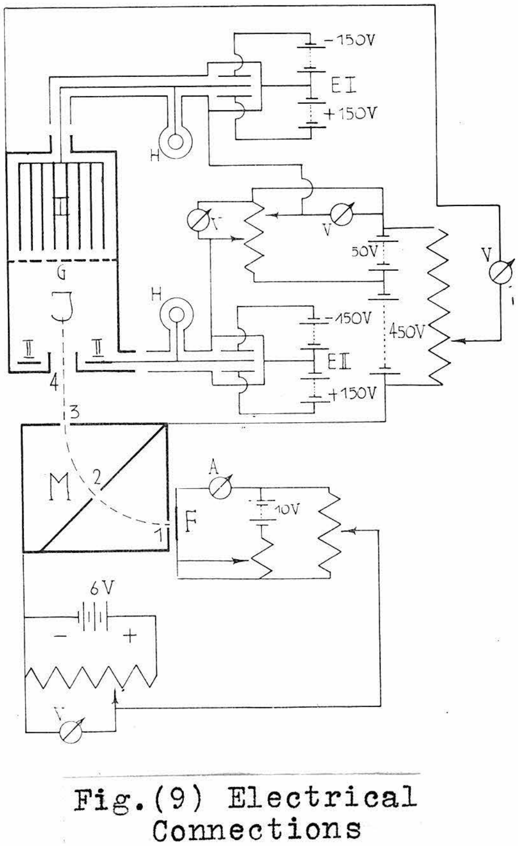

Fig.(9) Electrical Connections

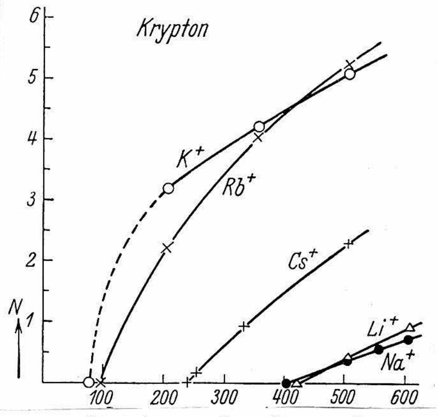

Fig.(11) N in krypton.

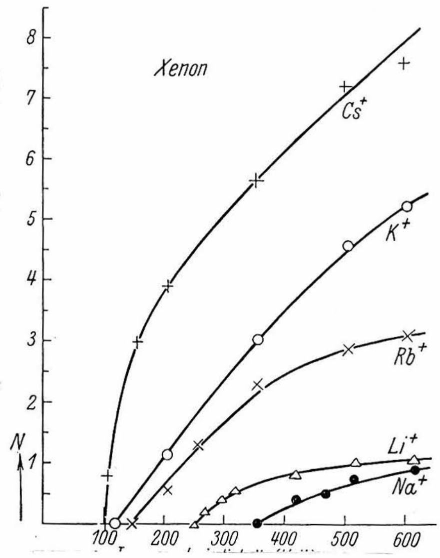

Fig.(12) N in xenon.

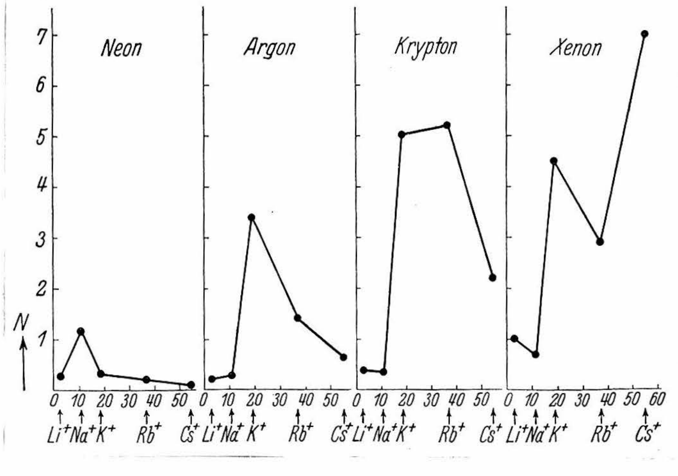

Fig.(13) N as a function of atomic number.

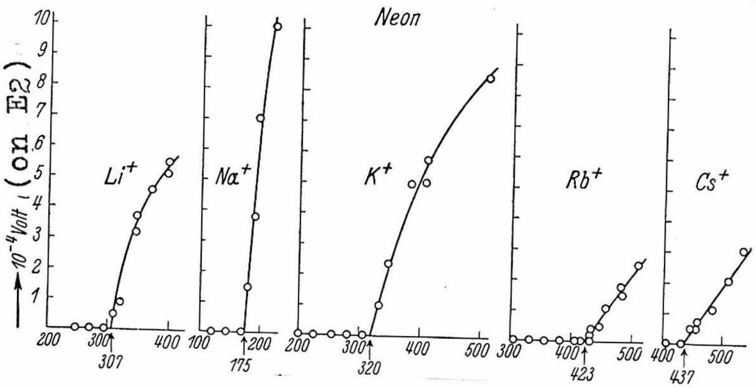

Fig.(14) Insetting potential in neon.

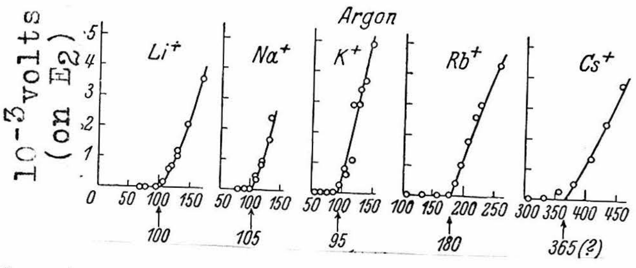

Fig.(15) Insetting potential in argon.

	Li	Na	K	Rb	Cs
Ne	307	**175**	320	423	437
A	100	105	**95**	180	365 (?)
Kr	420 (?)	400 (?)	**80**	100	143
Xe	250	360 (?)	120	145	**105**

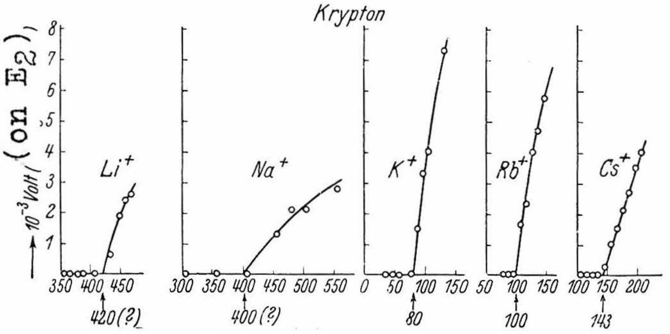

Fig.(16) Insetting potential in krypton.

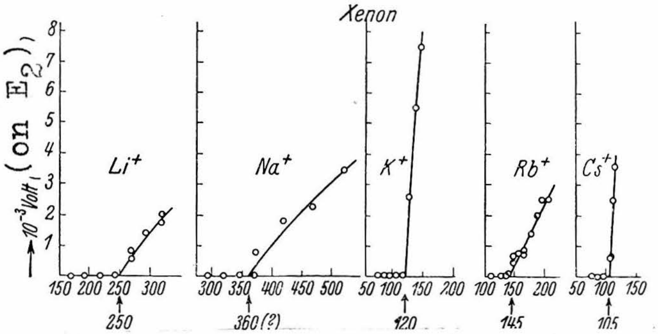

Fig.(17) Insetting potential in xenon.