IONIZATION OF GASES BY POSITIVE IONS

By Richard M. Sutton

Abstract

With a tube of simple design, positive ions of potassium are driven by controllable accelerating potentials up to 750 volts into neon and argon at various pressures. Small collecting potentials are adjusted in such a way as to eliminate practically all secondary effects due to the ions, enabling the collection of any electrons liberated by ionization in the gases. Pressure ranges between 0.05 and 1 mm give definite variation of ionization with pressure. Curves are given showing the variation of ionization with pressure and the number of new ions formed per positive ion per cm path reduced to 1 mm pressure. Ionization by this process does not offer a sharp initial point, but a measurable amount is present in neon at 100 volts, and in argon between 100 and 150 volts. The efficiency of the effect is decidedly less than for electron bombardment in these gases; it is several fold greater in argon than in neon. In neither gas has the efficiency reached a maximum at 750 volts, although there is evidence in the case of argon that the maximum efficiency may be found at a slightly higher accelerating potential. The pressure range within which the ionization effect shows itself is higher than should be expected from kinetic theory, which seems to indicate the presence of long mean free paths for the positive ions in accord with results of other observers using magnetic analysis apparatus.

SEVERAL attempts have been made in the past to determine whether positive ions of small energy are effective in ionizing gases. There seems to be considerable disagreement in the results of these attempts and few unambiguous positive results. L. B. Loeb[1] has cited fairly complete references to the subject of positive ion ionization; the reader is referred to his paper for a summary of the previous work in this field. It is well known that canal rays which have passed through potential drops of 10,000 volts or more are capable of producing intense ionization; the theory of this process has been treated by Bohr,[2] J. J. Thomson,[3] and others, particularly for the case of alpha-particles. Ionization in this region seems to be due largely to the action between electric charges in which the relative masses of the impacting bodies plays comparatively small part. In the range below 1000 volts, the evidence is not so clear. The present paper aims to set forth the results of some new experiments on ionization by positives. These experiments show definitely that potassium ions can produce ionization in argon and neon by accelerating potentials as low as 100 volts.

There are three chief secondary effects produced by positive ions which must be accounted for in order to separate ionization from masking phenomena: secondary emission of electrons from metal surfaces in the tube, as treated by A. L. Klein,[4] W. J. Jackson,[5] and others; reflection of positive

[1] L. B. Loeb, Science **66,** 627 (1927).
[2] Bohr, Phil. Mag. **30,** 581 (1915).
[3] J. J. Thomson, "Electricity in Gases," p. 370.
[4] A. L. Klein, Phys. Rev. **26,** 800 (1925).
[5] W. J. Jackson, Phys. Rev. **28,** 524 (1926); **30,** 473 (1927).

ions from the metal parts, studied by G. E. Read,[6] and R. W. Gurney,;[7] and photoelectric effect of excited atoms upon the walls of the tube and the metal parts. Many experimental studies of ionization have been diverted to the study of these effects. W. J. Hooper[8] made attempts to ionize hydrogen with sodium positive ions up to 900 volts and reports negative results. A more recent attempt with hydrogen by Gurney[9] using 7000 volts accelerating potential for K^+ ions, leads to rather inconclusive results. The author's own efforts with hydrogen led to confirmation of Hooper's results. However, in argon, neon, oxygen, and air definite evidence of ionization was found. The efficiency of the process is very low compared to ionization produced by electrons of the same kinetic energy. This difference is due, no doubt, to the relatively large mass of the positive ions and their complex structure which diminishes the probability of transferring sufficient energy upon collision to produce ionization. It is particularly improbable that the energy transferred should go into a single electron, rather than into the change of kinetic energy of the bombarded gas molecule as a whole. In view of the fact that argon gives a much larger effect than neon, it seems likely that the probability of ionization is dependent to some extent upon the number of electrons in the bombarded atom. This point will be tested by the use of other gases.

Apparatus

The tube used in these experiments is shown in Fig. 1. It is an adaptation of a tube constructed in the Norman Bridge Laboratory after a plan drawn up and devised by Dr. Millikan and Mr. Max Wehrli. The source of positive ions was a platinum filament situated in a semicylindrical porcelain trough, coated with a few mg of iron oxide catalyst developed by C. H. Kunsman and described in previous papers. Potassium positive ions from this source were sent by an accelerating potential V_a from the heated anode F, through a 2 mm hole in the cathode C, situated approximately 3 mm above the filament. The cathode was designed completely to enclose the source, thus preventing the escape of positive ions in any but the desired direction. The positives were kept from reaching the collector plate S by means of a small projecting ridge on the cathode which protruded through a circular hole in the collector. One centimeter above the cathode was a wide-meshed grid which was kept constantly at the

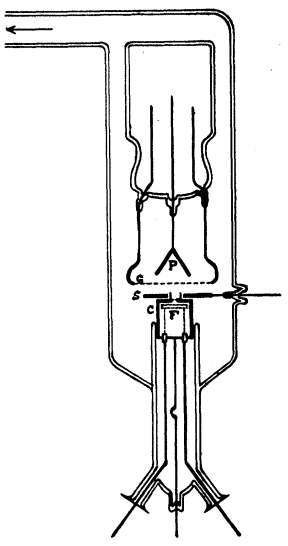

Fig. 1. Positive ion ionization tube.

[6] G. E. Read, Phys. Rev. **31,** 629 (1928).
[7] R. W. Gurney, Phys. Rev. **32,** 467 (1928).
[8] W. J. Hooper, J. Franklin Inst. **201,** 311 (1926).
[9] R. W. Gurney, Phys. Rev. **32,** 795 (1928).

potential of the cathode (ground), so that the space between C and G was field-free except for the bias voltage applied to the collector, never in excess of 13.5 volts. Above the grid was a nickel plate P made in V-shape to prevent reflection of positives. This plate was kept at positive 9 volts to prevent the escape of secondary electrons; this positive potential did not seem to increase the amount of reflection of positives from the plate, as might have been expected to follow. A measureable amount of reflection was found, but this was of small amount and appeared to reach a maximum in the region between 75 and 100 volts, just before ionization set in.

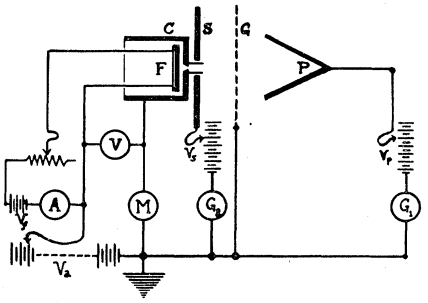

Fig. 2. Wiring diagram for positive ion apparatus.

The electric connections are shown in Fig. 2. A number of different combinations of grid, plate, and collector potentials were tried, but the system shown in the diagram proved most successful since it enables one to reduce the secondary effects to a minimum and collect any products of ionization formed. V_p was generally 9 volts positive to prevent secondary electrons reaching S; V_2 was always kept approximately 4.5 volts higher than V_p, so as to collect any electrons liberated between G and S. The only electrode from which electrons might reach S directly was the grid. The area of metal presented by it to the positive ion stream was exceedingly small. The primary ion current arriving upon the plate, I_p, was recorded by galvanometer G_1 having a sensitivity approximately 10^{-9} amp./mm. The electron current to S, I_2 was measured by a higher sensitivity galvanometer G_2 (10^{-10} amp./mm.) The heating current to the filament, usually about 7 amperes, was supplied by a heavy duty storage battery. It was easy to get pure positive ion emission as high as 10^{-6} amperes, but lower emission was usually used to insure steadiness of the source.

A two-stage mercury diffusion pump backed by a Hyvac served to reduce the pressure to at least 10^{-5} mm whenever desired. Pressures were read on a McLeod gauge connected to the apparatus between the pumps and liquid air trap. Liquid air or solid CO_2 were used at all times to exclude water and mercury vapor. The neon and argon were purified by sputtering for hours at low pressure in a magnesium arc. When clean, they could be admitted to any desired pressure into the experimental tube after the tube was separated from the pumps by a mercury cut-off.

Method of Measurement and Results

Several runs were made to determine what effects of secondary emission and reflection were present. In general the results of these runs confirmed previous observations on the subject. It was found that both effects could

be observed when the potentials of the electrodes were adjusted favorable to them. Fig. 3 indicates the amount of both these effects present at low pressure: Curve 1 showing approximately 7 percent secondary emission at 750 volts accelerating potential with the potential of plate and collector arranged to get a maximum effect; Curve 2 showing less than 1 percent reflection with plate and collector potentials reversed; Curve 3 showing the amount actually present in the experiments when plate and collector potentials were both positive. It will be seen that positive reflection is greater at low values of V_a and secondary emission relatively greater in the higher range, but the total secondary effect at any voltage does not exceed 1 percent of the primary ion emission. The steep increase of Curve 2 near the zero of voltage is natural, as here the accelerating potential of the positives is less than the retarding potential upon the plate which causes the whole ion stream to fall upon the collector S. Both reflection and secondary emission could be increased by cleaning the electrodes, but it was found favorable to let them absorb gas and thus reduce the effect due to them to a minimum. Between runs with different gases, the tube was thoroughly baked out; it was frequently evacuated to very low pressure during the experiments to prevent the accumulation of contaminations emitted by the filament or other sources.

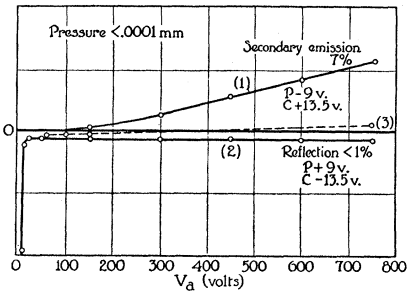

Fig. 3. Reflection and secondary emission at low pressure. Curve 3 shows effect present when $P=+9$, $C=+13.5$ volts.

The accelerating potential, V_a, applied between the anode and cathode, could be varied continuously from zero to 750 volts, the maximum employed in these observations. V_p and V_s were maintained constant during each run and were kept purposely small so as to minimize the possibility of ionization by electron impact. It is important to note that the maximum electron voltage possible within the region where ionization was measured did not exceed 13.5 volts, which is not sufficient to ionize either argon or neon. By maintaining V_s 4.5 volts higher than V_p, reflected ions were kept from reaching the collector unless they were reflected with energy in excess of 4.5 volts. The shape of the plate P also helped to prevent reflection in the direction of S.

Fig. 4 shows curves obtained from neon at various pressures. The curve for the lowest pressure indicates what part of the effect was due to secondary effects other than ionization; for at pressures as low as 0.0001 mm relatively few impacts between positive ions and gas atoms would occur. Any effect present at this pressure must then be due to electrode emission, and it might be reasonable to expect that it is at least as large at this pressure as it would be at higher pressures. As the gas pressure is raised, a distinct increase in the observed current to S is apparent. These curves are obtained by varying V_a, observing at the same time the values of G_1 and G_2 currents. The ratio

of currents to the two galvanometers, I_s/I_p, is plotted against the accelerating potential.

I_p represents the current of initial positive ions from the filament to fall upon the plate, diminished by any reflection of positives or by the arrival of electrons upon the plate due to ionization in the region between G and P, since the potential upon P is such as to collect electrons. Any secondary electrons which succeed in getting away from P would tend to increase the observed value of I_p. I_s represents electron current to the collector plate. Should scattered positives succeed in reaching S against the 13.5 volt retarding field, they would cause a decrease in I_s, or a complete reversal as may be noted over a short range of voltage just before ionization sets in.

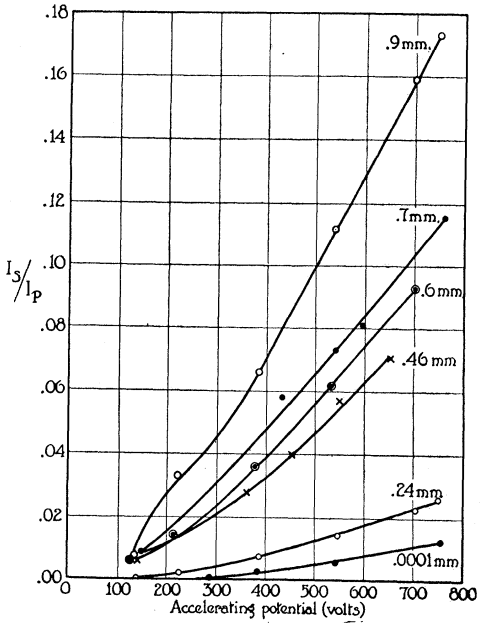

Fig. 4. Curves showing ionization in neon at several pressures. (Ratio of current to collector to current to the plate, plotted against accelerating potential).

Any electron current reaching S must come from the products of ionization between G and S, or from secondary emission from the grid. The latter effect should be a maximum at low pressure, whereas the former will show definite dependence upon the pressure. The ratio of I_s/I_p should therefore be a measure of the ionization produced per positive ion emitted through the hole in the cathode. That this ratio depends directly upon the gas pressure and upon V_a, but is essentially constant for wide variations in I_p, is considered evidence of an ionization effect apart from secondary effects upon the electrodes. An increase of one hundred-fold in the value of I_p causes less than 3 percent increase in this ratio; it was found possible to maintain I_p nearly constant over long periods of time so that error from this

source is negligible. The purity of the gases used should exclude the presence of any appreciable amount of ionization by collisions of the second kind such as observed by G. P. Harnwell[10] in these gases by magnetic analysis of the products of ionization.

Argon was treated in similar fashion to neon giving a series of curves very similar to those in Fig. 4, but showing several times as intense ionization for the same accelerating potentials. This fact will appear evident in the average curves shown in Fig. 5. It was found that ionization in argon and neon set in at approximately 100 volts (perhaps a trifle higher for argon), which is over five times the *kinetic energy* necessary to produce ionization in these gases by electrons. The actual *velocity* of the K^+ ion at 100 volts is, however, equivalent to that of a 0.00135 volt electron. It seems of interest

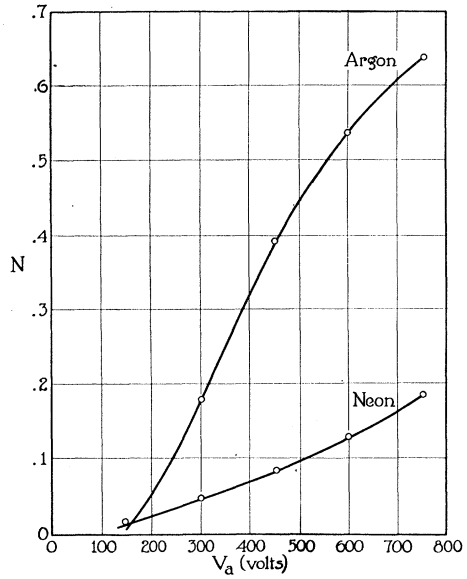

Fig. 5. Plot of N, the number of ions formed per initial positive ion per centimeter path, reduced to 1 mm pressure.

to compare the efficiency of positive ionization with that produced by electrons in the manner used by K. T. Compton and Van Voorhis.[11] Fig. 5, therefore, combines the results of a large number of curves similar to those in Fig. 4 for each gas taken at various pressures, reducing to a path length of 1 cm and a pressure of 1 mm. Comparing these curves with similar curves given by Compton and Van Voorhis, it will be seen that electrons are most effective ionizers in neon at 340 volts and in argon at 140 volts; whereas positive ions at 750 volts have not reached a maximum. The curve for argon indicates that this maximum efficiency might be approaching; it would be of interest to extend the voltage range to see whether the curves for positive

[10] G. P. Harnwell, Phys. Rev. **29**, 583 (1927).

[11] K. T. Compton and C. C. Van Voorhis, Phys. Rev. **26**, 436 (1925).

ion bombardment have the same characteristics as those for electrons. Even at 750 volts, the efficiency observed is less than 7 percent of the efficiency recorded by Compton and Van Voorhis, at the maxima for these gases, using electrons as the ionizing agent.

Although commercial oxygen, hydrogen, and air were used in similar fashion to argon and neon, the results are not plotted since no effort was made to purify these gases. Positive results of ionization were found in the case of oxygen and air, whereas any such effect in hydrogen was not observable over the secondary effects of the ions on the electrodes. It appears doubtful that a heavy positive ion can impart sufficient energy to a hydrogen molecule to ionize it without going to considerably higher accelerating potentials. Pressures in hydrogen were used high enough to show ample effect in the other gases, and accelerating potentials up to the arcing voltage were used without evidence of ionization by the positives. It might be of interest to repeat these experiments using lighter positive ions, as kinetic considerations would indicate a greater probability of transfer of energy to the hydrogen in sufficient quantity to produce ionization if the impacting ion were of smaller mass than potassium. However, if the amount of ionization depends upon the number of electrons in the atom bombarded, this argument will not hold and no appreciable increase of ionization would be found from the use of a lighter bombarding ion. This point is one which should be directly settled by experiment.

Discussion

The sensitivity of the method used in these experiments does not permit the location of an exact ionization potential for positive ion bombardment, nor would one expect to find an exact voltage at which the effect sets in. The very nature of the impacts between bodies as complex as a potassium ion and an argon or neon atom would at least blur the point at which ionization sets in. This has been pointed out by J. Franck,[12] Joos and Kulenkampf,[13] and C. Eckart,[14] who have treated the theoretical aspects of this problem. The observed value of 100 volts is slightly higher than Franck postulates for ionization by positive ion impact, given the proper sequence of events favorable to ionization, but it is at least in the same order of magnitude. It is possible that more sensitive methods of measuring the current to the collector S would push this value down a few volts by enabling one to observe the less probable impacts resulting in ionization. However, the slope of the curves as (in Fig. 5) they approach the zero axis indicates a fairly sharp origin of the effect. Any ionization which escaped detection must have been less than 0.001 as intense as the primary positive beam.

It will be observed in Fig. 6, in which the ionization is plotted as a function of the logarithm of the gas pressure, that the effect does not appear in any appreciable extent until the pressure reaches 0.05 mm, at which pressure

[12] J. Franck, Zeits. f. Physik **25,** 312 (1924).
[13] Joos and Kulenkampf, Phys. Zeits. **25,** 257 (1924).
[14] C. Eckart, Science **62,** 265, (1925).

the mean free path of a potassium ion according to kinetic theory is of the order of 1 mm. A large effect is still evident above 0.5 mm pressure, with a corresponding reduction of mean free path. At 0.3 mm pressure more than 50 percent of the ions emitted by the filament succeed in getting through to the plate, which according to kinetic theory would mean approximately 400 collisions per ion without neutralization or appreciable loss of momentum in the forward direction since each positive ion must go against a retarding field of 9 volts to reach the plate. It seems therefore probable that these positive ions have considerably longer mean free paths without suffering appreciable scattering or neutralization than would be expected on kinetic theory. Striking as this result may be, it appears to be in accord with the results of Kennard,[15] and Durbin,[16] who examined this point more carefully by magnetic analysis apparatus and were thus able to measure the amount

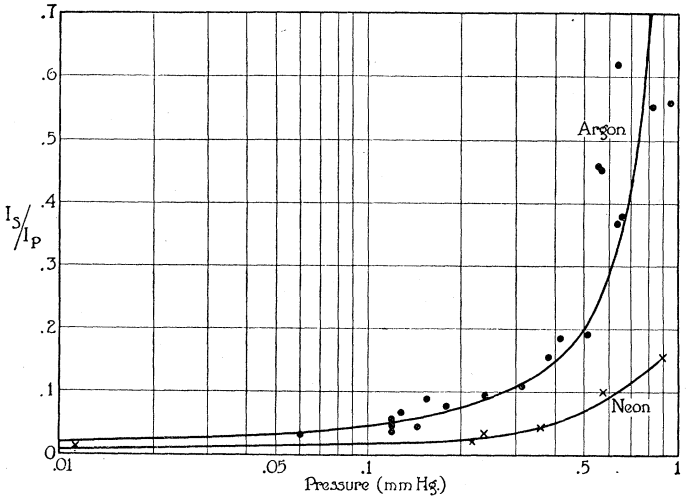

Fig. 6. Variation of ionization in neon and argon plotted against the log of gas pressure.

of loss from the original beam and the loss of energy per ion in traversing the long paths used in their apparatus. It does not agree so well with the results of Harnwell,[17] who used a method which seems less reliable in testing this point than the method of Kennard and Durbin. The writer's results call for the transfer of a larger fraction of the ion's energy upon collision than is allowed in Harnwell's conclusions, as his available 0.002 for neon and 0.005 for argon is not sufficient to cause ionization in either gas within the range of voltages used in this experiment. It seems worth while to investigate this point regarding the mean free path farther and to find, if possible, some adequate explanation for it.

[15] Kennard, Phys. Rev. **31,** 423 (1928).
[16] Durbin, Phys. Rev. **30,** 844 (1927).
[17] Harnwell, Phys. Rev. **31,** 634 (1928).

Neon and argon may be particularly favorable gases to employ since they both have metastable states of long duration; hence there may be some possibility of ionization by multiple impact. The high energy value of these metastable states might cause intense photoelectric effect upon the metal parts in the tube. Any such effect upon the plate would be negligible in aiding electrons to reach S since the potential V_p plus the work function of the metal would exceed the energy available from radiation due to an excited state. Photoelectric effect upon the grid might liberate a few electrons to the collector plate S.

A careful analysis of sources of current to the collecting electrode brings the author to the following conclusions: i) that secondary emission from the metal parts, beyond a possible 2 or 3 percent of the observed effect, is eliminated; ii) that reflection of the positive ions plays a minor part and is evident only within the range from 50 to 100 volts before ionization sets in; iii) that photoelectric effect upon the electrodes (except the grid) plays no effective part by reason of the bias potentials, V_p and V_s used; iv) that ionization by collisions of the second kind plays a negligible part so long as the gases are pure; v) that ionization by electrons liberated from the metal parts cannot take place since there are no potentials in the upper part of the tube high enough to give electrons sufficient energy. Therefore, the currents recorded upon the collector, with the exceptions just noted, are due to electrons liberated within the gas itself by positive ion impact.

It is hoped to extend these experiments to other sources of positives and other gases, and it would seem desirable also to increase the range of potentials up toward the canal-ray region to obtain fuller knowledge of the effectiveness of positive ions as ionizing agents. Any information thus obtained must play a real part in solving the problems of gas discharges.

The writer wishes to express his appreciation of the helpful interest given by Dr. R. A. Millikan during this work, and of the critical suggestions offered by Mr. Willy Uyterhoven.

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