SEPTEMBER 1, 1932 PHYSICAL REVIEW VOLUME 41

The Ionization of Neon and Argon by Positive Alkali Ions of Energies from 650 to 2000 Volts

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(Received July 14, 1932)

With an apparatus of new design the study of the ionization of neon and argon by positive alkali ions has been extended to accelerating potentials as high as 2000 volts. The results obtained are in good quantitative agreement with the previous work at the low potentials. In a number of cases the efficiency of ionization reaches a maximum at accelerating potentials less than 2000 volts.

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.

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 in 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.[2]

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

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[1] Klein, Phys. Rev. **26**, 800 (1925).

[2] Richard M. Sutton, Phys. Rev. **33**, 364 (1929).

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 devised 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[3] in 1930 and 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. The investigations in xenon and krypton showed that this statement is not strictly true, though it holds in most cases. The fact that potassium is equally efficient an ionizer of krypton as is rubidium and the fact that potassium is more efficient as an ionizer of xenon than is rubidium brings one to the conclusion that so simple a statement falls short of the observed phenomena. However, an 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 cross-section values[4] are a trifle better.

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[3] Sutton and Mouzon, Phys. Rev. **35,** 694 (1930); Sutton and Mouzon, Phys. Rev. **37,** 319 (1931).

[4] Ramsauer and Beeck, Ann. d. Physik **87,** 1 (1928).

Table 1 gives the values of the probability of ionization thus computed. 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, the mean free path used could account for a wider variation than is found. If one considers the ionization as due largely to the kinetic impact of two elastic bodies, as does Dr. Fritz Zwicky[5] of this Institute, it is not surprising that the probabilities of ionization for the alkalis in their neighboring noble gases are about the same.

TABLE I.

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

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 used are low. A summary of these findings appeared in the Physical Review.[6] A more detailed account was given in two articles in the Annalen der Physik.[7]

Unsuccessful attempts to use positive alkali ions of energies greater than 500 volts were made by Sutton and the writer, and later by Beeck and the writer. The apparatus used in the former case was limited because of a gas discharge taking place between the filament and cathode[3] at the higher potentials. Measurements were actually made up to 750 volts. In the latter case a very large reflection of positive ions occurred at the higher potentials.

A new apparatus has been built which is more suitable for the work and which gives quite satisfactory results. A further difficulty was encountered with the present apparatus which was masked by the other effects in the earlier pieces of apparatus at velocities in excess of 750 volts. This was the problem of secondary emission from the metal parts. By applying a potential of about 9 volts it is possible to prevent the escape of electrons from a metal when the bombarding ion has an energy of less than 600 volts. However, for greater energy positive ions, some of the electrons ejected seem to have an energy of much more than 9 volts. With proper adjustments the secondary emission was finally reduced to such a low value that, by making corrections for it, quite good results were obtainable.

Fig. 1 is a cross section of the apparatus. The source of positive ions, F, is a platinum foil coated with Kunsman catalyst. (The filament holder is not

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[5] Zwicky, Proc. Nat. Academy of Sc. **18,** 314 (1932).

[6] Beeck and Mouzon, Phys. Rev. **38,** 967 (1931).

[7] Beeck and Mouzon, Ann. d. Physik **11,** 737, 858 (1931).

indicated in the drawing.) Ions of the five alkalis were thus obtained. The most satisfactory method of coating the filament with the source material was found to be as follows: The catalyst was mixed with paraffin oil to facilitate spreading it on the surface of the foil. Successive thin coats were painted on the foil, the source being heated to a yellow heat in an atmosphere of hydrogen after each coat. The result was that the catalyst adhered very firmly to the foil and no difficulty was encountered with the catalyst falling off when it was mounted upside down in the filament holder. This would occur if the source were not reduced in steps as was indicated.

The ions are accelerated to a grid and pass through the magnetic analyzer through 1×6 mm slits, S_1 and S_2. The Armco iron pole pieces of the mass spectrometer are separated 5 mm by brass spacers. The copper plate, B, is supported on A by means of a glass tube which insulates the two. The positive ions enter the ion chamber through slits, S_3 and S_4. These slits are 1×6 mm and 0.5×6 mm, respectively. The channel shown prevents any of the initial positives reaching the electron collector, C. A small ring is shown projecting into this channel at its base. This is to prevent as many ions as possible from striking the walls of the channel from which secondary electrons might easily be ejected. The joints of glass to copper are made with picein wax.

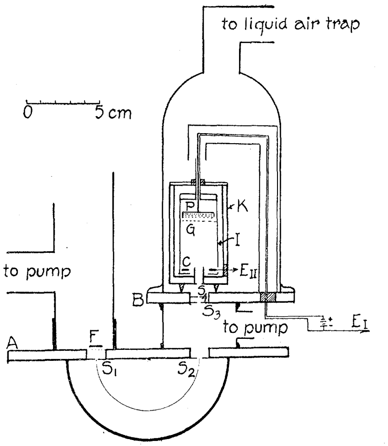

Fig. 1. Cross section of magnetic analyzer and ionization chamber.

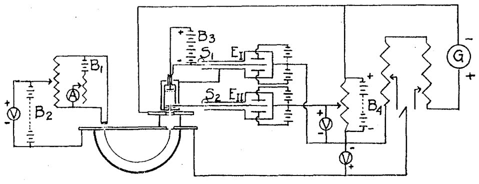

Fig. 2. Electrical connections.

A small bell jar sealed with wax to the ground plate, B, contains the ionization chamber and makes it easily accessible. The tube connected to the top of the bell jar leads directly to a liquid air trap which freezes out the vapors present.

The ionization chamber is surrounded by a soft iron cylinder K to shield it from the stray magnetic field. The whole rests on redminol feet, insulating it from the plate B. The collector for the initial positive ions is of a different design from that previously used, consisting of the collector P and the brass cylinder I. The major part of the beam is collected on P. Any alkali ions scattered by the gas are caught on the walls. The collector P is a brass box, 3 mm deep, containing two 0.5 mm mesh screens inside and one 2 mm mesh screen at the opening. This cage effect is very successful in preventing the reflection of the initial positive beam which proved troublesome at the high energies in the previous apparatus.[8] The collection of all the positive ions entering the chamber, including those scattered by the gas, affords more accurate measurements than previously. However, the agreement of the results obtained with this apparatus with those obtained with the earlier pieces of apparatus indicates that the scattering is very small at the pressures used. The cage P is maintained at a potential of 18 volts above I by means of a small battery inside the shielded electrometer lead. For accelerating potentials in excess of 900 volts this is no longer sufficient to retard all of the secondary electrons. It is therefore necessary to make a correction for these ejected electrons.

The electron arising between the grid G and the upper end of the channel are collected on the plate C. Any other electrons arising from the bombardment of the metal walls are also collected there. It is true that the positive gas ions arising as products of ionization by the alkalis are measured with the initial positive ions, but the error introduced by this is very small since these are in general less than one percent of the value of the initial positive beam.

A diagram of the electrical connections is shown in Fig. 2. The filament is heated by means of the battery B_1. An initial acceleration of 54 volts is applied at the center of a large resistance across the filament by means of the battery B_2. A second acceleration is applied between plates A and B after the ions have passed through 180° in the magnetic field. This acceleration is variable as is shown, the potential being derived from the 2000 volt generator, G. A third acceleration of 48 volts from B_4 exists between the soft iron cylinder and the plate, B. This last acceleration is thus applied so that no electrons arising from the slits or from the gas streaming through the channel may enter the ionization chamber and be collected on C.

The cage P is maintained at 18 volts positive with respect to the cylinder I by means of the battery B_3 in the electrometer lead. The electrometer E_{I} measures the initial positive beam. The collector C for the electrons liberated from the gas is maintained at a potential positive with respect to the surrounding cylinder I by means of the battery B_4. This potential has to satisfy two conditions. It must be high enough so that all the electrons liberated between C and G are collected, but it must be less than the electron ionization potential of the gas. The collector C has to be large enough to make this possible. (This is the same restriction as existed in all of the previous work.) By plotting the charge collected on C against the collecting potential applied on C, for a given acceleration of the alkali, one can determine whether this condition is satisfied. 12 volts were found suitable for the work in argon and 15 volts for neon. The electron charge on C is measured by electrometer E_{II}. The two electrometers are of the string type. All leads to them were carefully insulated with amber, and carefully shielded. Switches S_1 and S_2 are electromagnetically operated *grounding* switches for the two instruments.

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[8] Beeck, Ann. d. Physik **6**, 1001 (1930).

The gas is admitted to the ionization chamber from a reservoir through a fine capillary and is continuously pumped through, assuring purity. The pump leads are as indicated. The difference in pressure between the ionization chamber and the mass spectrometer is such that with the pressure as much as 10^{-2} mm in the chamber, a large number of positives are still undeviated from their path. Pressures are measured on a McLeod gauge at intervals during a run. The time of each reading of the electrometers is recorded and the pressure of the gas at that time may be obtained from a pressure-time graph. The change in pressure never amounts to more than 1.5×10^{-3} mm in ten minutes. The time of charging up of the electrometers is between 5 and 10 seconds, so that the change in pressure during that period is negligible. The pressure used were between 2×10^{-3} and 7×10^{-3}. The chance of multiple collisions is therefore small.

The ratio of the effective capacities of the two collecting systems with their leads and electrometers must be known in order to secure the true ratio of the charges collected. Obviously. there is an inductive effect of one system on the other, since the collector of the initial positive ions surrounds that of the electrons liberated from the gas. However, in this apparatus the inductive effect of the system of electrometer E_{II} on the system of E_{I} is very small. Therefore, the ratio of the capacities can be measured by simply putting a charge on E_{I} and sharing it with E_{II}, the deflections on E_{I} being measured before the charge is shared and immediately thereafter. The potential originally applied on E_{I} can be measured by a bridge, so that all of the data are obtainable to give the ratio of the capacities, C_1/C_2 by the formula: $C_{\text{I}}/C_{\text{II}} = V_1'/(V_1 - V_1')$ where V_1 and V_1' are the potentials as read on E_{I} before and after the charge is shared with E_{II}, respectively. This ratio was found to be 3.38.

The actual measurements are taken as follows: With E_{I} and E_{II} grounded the filament is turned on; S_1 and S_2 are then opened simultaneously. When the charge has reached a satisfactory value, the filament switch is opened and the deflection of E_{I} is read. S_1 is now closed, grounding E_{I}, and the deflection of E_{II} is read. This procedure is necessary since the relatively large positive charge on E_{I} induces a charge on E_{II}. E_{I} must, therefore, be grounded before the true electron charge on E_{II} can be measured. The whole process of taking one reading requires from 5 to 10 seconds only. However, at the high accelerating potentials the drift of electrometer, E_{II}, is sufficient in that length of time to require a correction. The results obtained speak for the validity of these methods employed in the measurements.

As was previously mentioned, a correction must be made for the secondary emission. Fig. 3 shows how this correction can be made. The value of the ratio of the total electron charge collected on C divided by the corresponding positive ion charge is plotted against the pressure. In Fig. 3, $N\times P$ represents this value multiplied by a constant. It is N, the efficiency of ionization (the number of electrons ejected from the gas per initial positive ion per cm path per mm pressure) that is finally desired, so that it is convenient to carry this multiplying constant. As is expected, if only single collisions occur, this ratio is a linear function of the pressure. The intersection of the lines with the axis of zero pressure gives the portion of $N \times P$ due to secondary emission only.

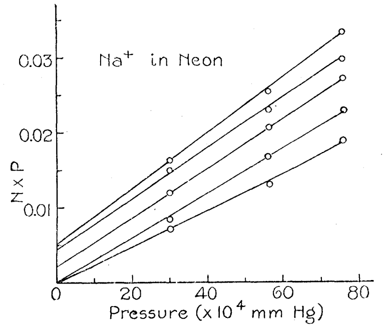

Fig. 3. Ratio of electron charge to positive ion charge as a function of pressure.

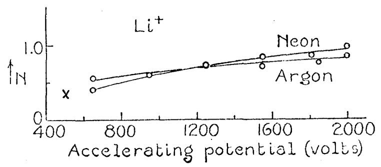

Fig. 4. Efficiency of ionization, N, of lithium in neon and argon as a function of accelerating potential.

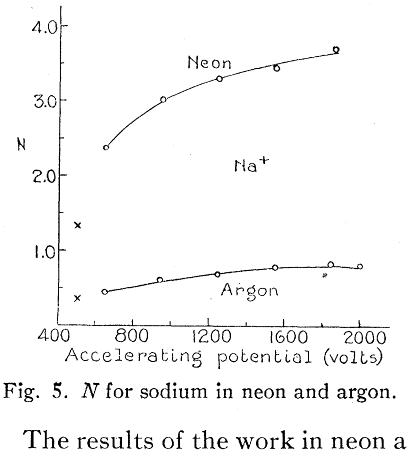

Fig. 5. N for sodium in neon and argon.

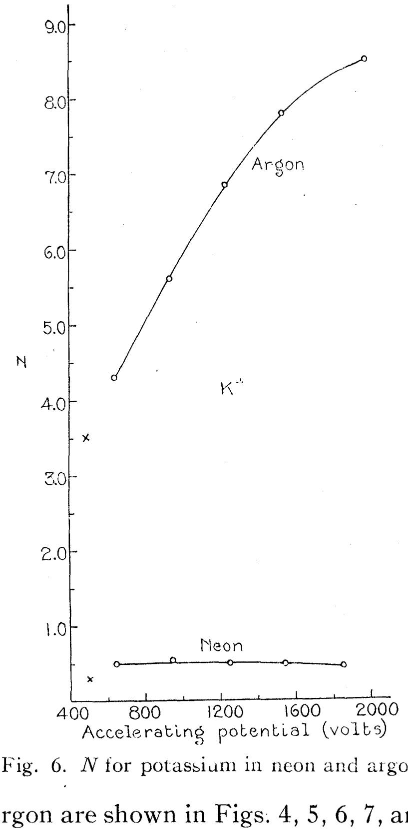

Fig. 6. N for potassium in neon and argon.

The results of the work in neon and argon are shown in Figs. 4, 5, 6, 7, and 8. The value of the efficiency of ionization, N, defined above is plotted against the accelerating potential. The crosses indicate the values obtained by Beeck[8] at an accelerating potential of 500 volts. It is seen that in nearly all of the cases the agreement is excellent. Not only that, but also the slopes of the curves are such that, if extrapolated, the curves would strike the axis in good agreement with the values of the insetting potentials obtained by Beeck and the writer.[6] [7] That is particularly noteworthy when one considers that the apparatus used in the two cases is quite different. Too much accuracy cannot be claimed for the lower efficiencies, since the secondary emission was a considerable part of the charge measured. The fact that rubidium and caesium show relatively large efficiencies in argon again makes one wonder what role the electron configuration plays, since a simple *mass effect* cannot explain this. It is interesting to note that all of the curves show a tendency toward reaching maxima if they have not done so already at these potentials.

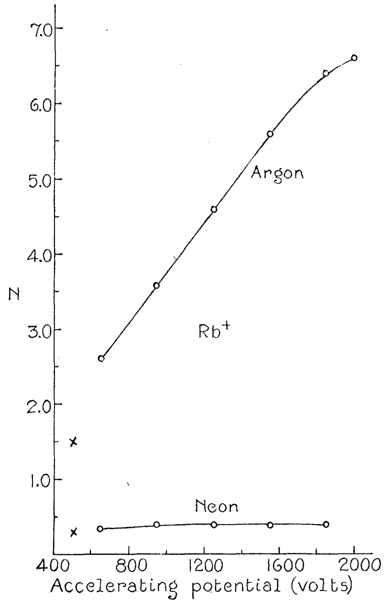

Fig. 7. *N* for rubidium in neon and argon.

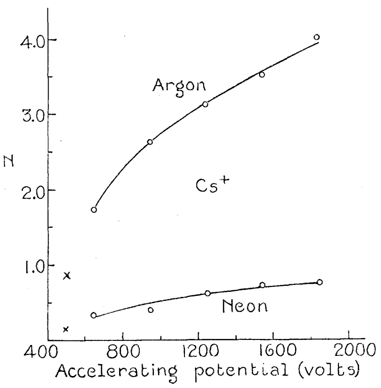

Fig. 8. *N* for caesium in neon and argon.

In conclusion, the writer wishes to express his appreciation for the interest of Dr. R. A. Millikan in this work and for the discussions with Dr. Otto Beeck concerning the whole problem.