IONIZATION POTENTIALS AND PROBABILITIES FOR THE FORMATION OF MULTIPLY CHARGED IONS IN HELIUM, NEON AND ARGON.

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Abstract

The multiply charged ions in helium, neon and argon have been studied with a mass spectrograph previously described. In helium the He^+ ion showed up strongly but only faint evidence for the formation of He^{++} was found and no quantitative data for its relative intensity could be obtained. Neon yie'ded the three ions Ne^+, Ne^{2+} and Ne^{3+} as the result of single electron impacts occurring respectively at minimum electron energies of 21.5, 63, and 125 volts. Curves which illustrate the efficiency for the formation of these ions expressed in number of ions per electron per cm per mm pressure at 0°C as a function of the electron velocity exhibit maxima for Ne^+ and Ne^{2+} of 2.75 and 0.16 at 150 and 250 volts respectively. In argon the five ions A^+, A^{2+}, A^{3+}, A^{4+} and A^{5+} were observed. The ionization potentials for the first four were found to be respectively, 15.7, 44, 88 and 258 volts for single impact. The efficiency curves show maxima of 11.4, 1.1 and 0.04 at 50, 115 and 250 volts for A^+, A^{2+} and A^{3+} respectively. In the curves for Ne^{3+} and A^{4+} are found several upward breaks beyond their ionization potentials which indicate other higher critical potentials for their formation.

Introduction

A METHOD of studying the multiply charged ions produced by electron impact in gases at low pressures has recently been described[1] and some results in mercury vapor and hydrogen have been reported. It is the purpose of the present paper to describe the results of a similar study of the ionization products in the rare gases—helium, neon and argon. Barton[2] has previously studied argon with a mass spectrograph. Certain improvements in the present method over those formerly employed have yielded new data, particularly in the experiments on neon and argon.

Apparatus and Procedure

The apparatus employed in this investigation was essentially the same as that used in the study of ions in mercury vapor and hydrogen.[1] The reader is therefore referred to this earlier work for a detailed description of the method. The gases were admitted to the apparatus through a fine capillary at one end of the tube and the pressure could be varied by opening or closing with a mercury cut-off constrictions of different sizes in the pumping line leading from the other end of the tube. The pressures found suitable varied from 5 to 50×10^{-5} mm Hg. Helium from a steel drum was purified by passing it over charcoal immersed in liquid oxygen. The neon and argon were admit-

[1] W. Bleakney, Phys. Rev. **34**, 157 (1929); **35**, 139 (1930); **35**, 1180 (1930).

[2] H. A. Barton, Phys. Rev. **25**, 469 (1925).

ted to the apparatus directly from the Pyrex containers supplied by the Air Reduction Company without further purification. A preliminary study of the ions showed the helium and argon to be quite pure while the neon contained a slight amount (less than one percent) of helium. There was always present in the tube, however, even before any gas was admitted through the capillary, traces of some impurities which were identified as hydrogen, water vapor, and carbon monoxide. The number of ions due to these impurities was very small compared to those of the gas under investigation necessitating a correction usually of about one percent in the cases of argon and neon. It was only in the determination of ionization potentials, where it was necessary to measure very small currents, that the impurities caused any trouble, and here their effect was minimized by proper adjustment of pressure and current density. In all the results presented in this paper the data have been corrected as far as possible for the effect of impurities.

RESULTS

Helium. The singly charged He^+ ion formed, of course, a very strong peak in the analyzer. Unfortunately for this work the H_2^+ ion has the same e/m as He^{2+} and since there was always, as mentioned above, a trace of hydrogen present in the tube it was impossible to get any quantitative measure of the number of He^{2+} ions produced. However, the evidence at electron velocities of several hundred volts pointed toward the existence of He^{2+} but certainly less than one percent of all the helium ions formed were doubly charged.

Neon. The three ions Ne^+, Ne^{2+}, and Ne^{3+} were found in neon and their ionization potentials were determined from the data shown in Fig. 1. Here the maximum heights of the peaks in the e/m analysis curves are plotted as functions of the electron velocity expressed in volts. With carbon dioxide snow on the trap a sufficient amount of mercury vapor remained in the tube to calibrate the voltage scale by means of the Hg^+ ion whose ionization potential was assumed to be 10.4 volts. Thus all of the ionization potentials could be measured without altering any of the conditions in the tube. The critical potentials obtained for ionization at single impact together with the estimated limits of experimental error are given in the second column of Table I. The agreement with the values calculated from spectroscopic data demonstrates the reliability of the method The experimental error increases with increasing charge on the ion because of decreasing intensity and lack of complete resolution

TABLE I. *Ionization potentials in neon for single electron impact.*

Ion	Experimental	Spectroscopic
Hg^+	10.4 volts	10.39[3] volts
Ne^+	21.5 ± 0.1	21.47[3]
Ne^{2+}	63.0 ± 0.5	62.4[4]
Ne^{3+}	125.0 ± 1.0	

[3] International Critical Tables VI, p. 71.

[4] H. N. Russell, K. T. Compton and J. C. Boyce, Proc. Nat. Acad. Sci. **14,** 280 (1928).

The curves for Ne^{2+} and Ne^{3+} shown in Fig. 1 have a peculiar shape, unlike the others, suggesting more than one process for the formation of these ions. Particularly in the case of Ne^{3+} the curve shows two definite upward breaks, the first occurring in the neighborhood of 143 and the second at about 157 volts. These are perhaps to be correlated with the energies necessary to remove different electrons from the neon atom. For instance it may require 125 volts to remove three $2p$ electrons, 143 volts to remove two $2p$ and one $2s$ at a single blow and 157 volts to remove one $2p$ and two $2s$ electrons in one group, all three processes resulting in Ne^{3+} ions.

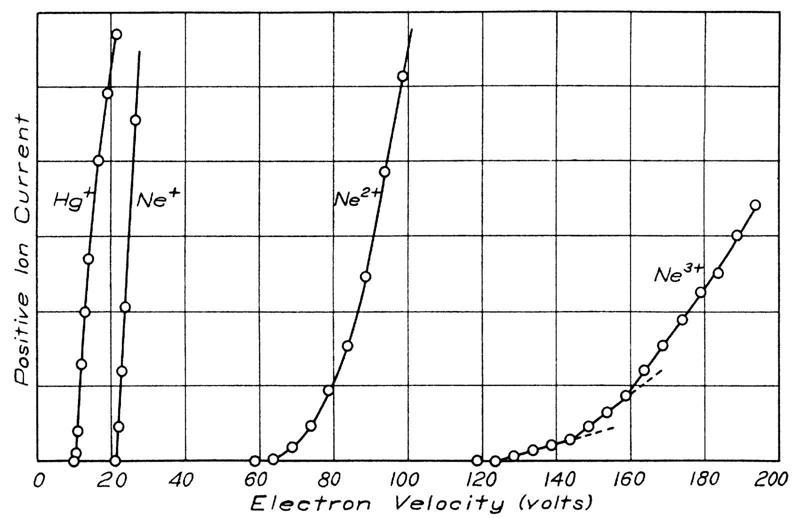

Fig. 1 Curves showing the ionization potentials in neon. The ordinate scale is an arbitrary one and differs for each curve.

The areas under the peaks in a set of runs carried out at various electron velocities were measured to determine the fractions of the total current carried by he several types of ions. The results are shown in Fig. 2 where the ordinates represent the percent of the total positive ion current to be assigned to the Ne^{+}, Ne^{2+} and Ne^{3+} ions. It will be noticed from the figure that beyond 200 volts approximately 88 percent of the current is made up of singly charged ions while doubly charged ions account for about 11 percent.

The data of Fig. 2 combined with the measurements of the total ionization given by Smith[5] enable one to calculate the probability of ionization for each type of ion. The result is obtained by multiplying the ordinate of Fig. 2 by the total ionization for that particular value of the electron velocity as given by Smith and dividing by the number of charges on the ion. Figure 3 shows the results of this calculation where the ordinates represent the probabilities of ionization expressed in numbers of ions per incident elecron per cm path per mm pressure at 0°C as a function of the electron velocity. The curves for Ne^{+} and Ne^{2+} exhibit broad maxima of 2.75 and 0.16 at 150

[5] P. T. Smith, see the preceding paper of this issue.

and 250 volts respectively while that for Ne^{3+} shows no maximum in the range studied.

Argon. A study of the mass spectrum of argon revealed the five ions A^{+}, A^{2+}, A^{3+}, A^{4+} and A^{5+} each one formed, it is believed as the result of a

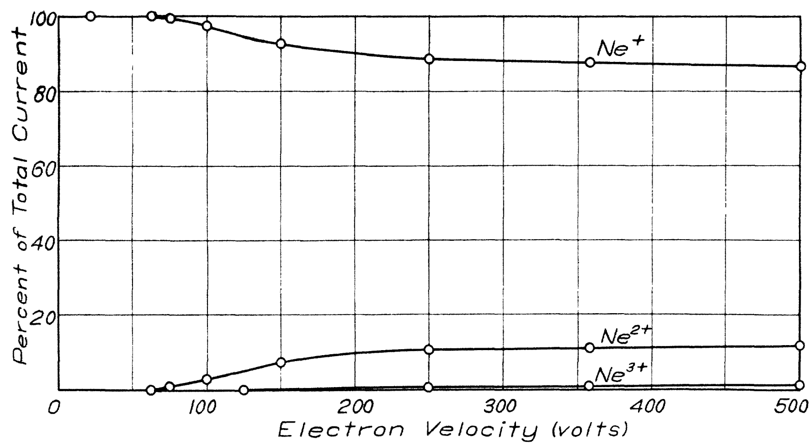

Fig. 2. Percent of total positive ion current ascribed to the different ions.

single electron impact. The intensity of A^{5+} was so small that no attempt was made to measure the number quantitatively. It can only be said that its formation certainly occurs at electron velocities below 500 volts. The ioniza-

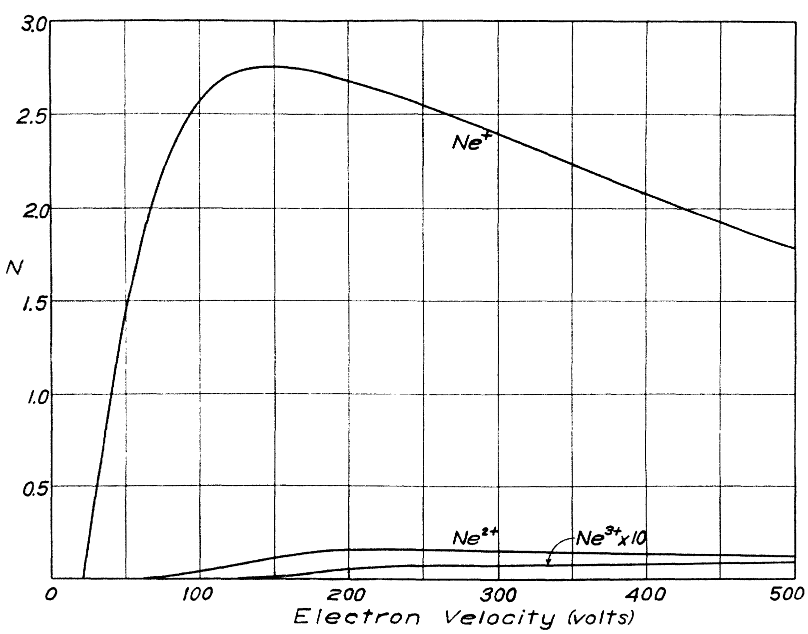

Fig. 3. Actual number of ions, N, formed per electron per cm per mm pressure at 0°C.

tion potentials for the first four ions were determined from the data shown in Fig. 4 and the values are given in Table II. It will be seen that the agreement with the spectroscopic values are quite satisfactory. The value 44.0 for A^{2+}

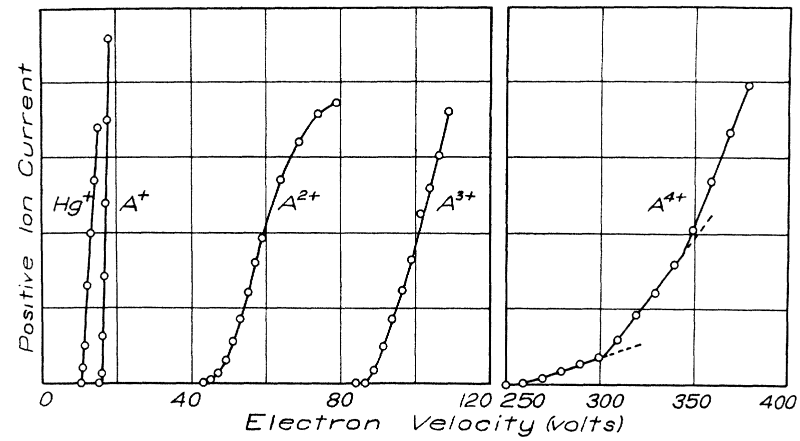

Fig. 4. Curves showing the ionization potentials in argon. The ordinate scale is an arbitrary one and differs for each curve.

checks quite well that found by Barton[2] which becomes 45.8 when his voltage scale is corrected to make A^+ appear at 15.7 volts.

TABLE II. *Ionization potentials in argon for single electron impact.*

Ion	Experimental	Spectroscopic
Hg^+	10.4 volts	10.39[3]
A^+	15.7±0.1	15.69[3]
A^{2+}	44.0±0.5	43.51[6]
A^{3+}	88 ±1	
A^{4+}	258 ±3	
A^{5+}	Less than 500	

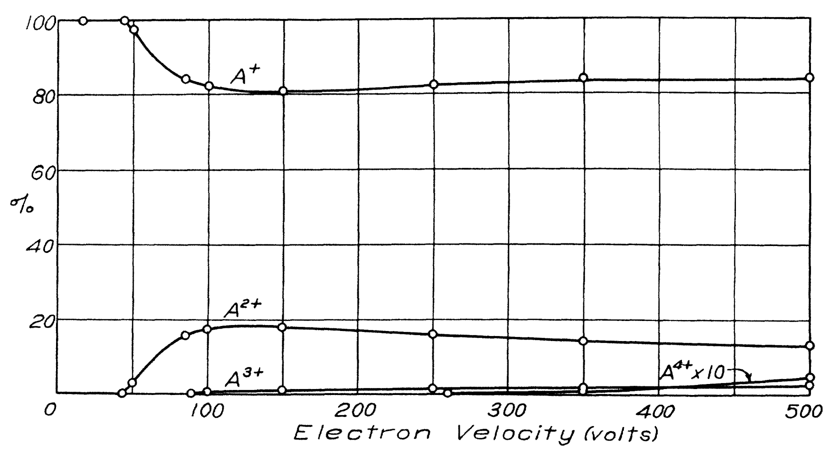

Fig. 5. Percent of total positive ion current ascribed to the different ions.

[6] K. T. Compton, J. C. Boyce and H. N. Russell, Phys. Rev. **32**, 179 (1928).

Like neon, the curves for the multiply charged ions in argon show peculiar shapes indicating more than one process of formation, and especially is this true of the fourth ion where upward breaks occur in the neighborhood of 300 and 340 volts. In all of the runs made these breaks consistently appeared but the values of the abscissas where they began did not check very well because of the difficulty encountered in holding the magnetic field perfectly constant. Hence the values given may be in error by several volts. It is hoped that these phenomena may be more carefully investigated in future work.

The fractions of the total positive ion current carried by the several ions are illustrated in Fig. 5. It appears that at least 80 percent of the current may always be ascribed, under the conditions of this experiment, to the singly charged ion in the range studied. Using again the data of Smith[5] the probabilities of producing the first four ions as a function of the electron velocity have

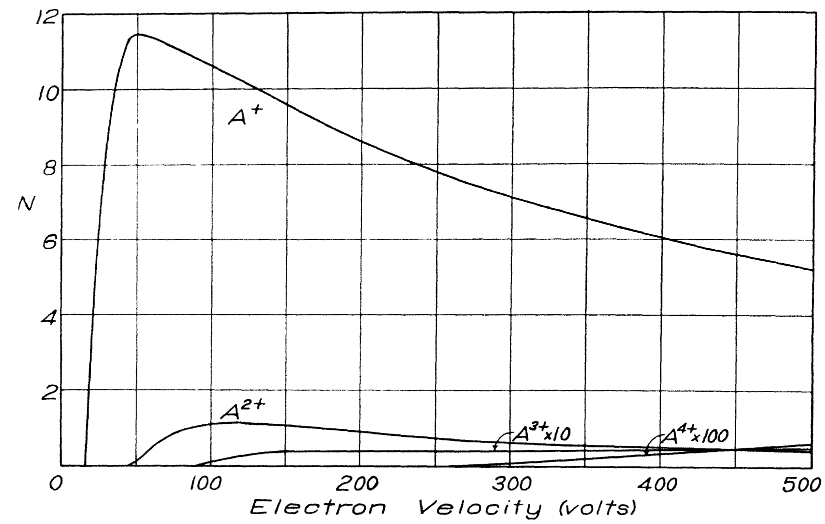

Fig. 6. Actual number of ions, N, formed per electron per cm per mm pressure at 0°C.

been calculated and are given by the curves of Fig. 6. The A^+ ion rises very sharply to a maximum value of 11.4 at 50 volts while the A^{2+} ion reaches a value of 1.1 at 115 volts. The number of A^{3+} ions shown only a very broad maximum of 0.04 beyond 150 volts and the A^{4+} curve continues to rise as far as 500 volts. The position for the maximum in the A^+ curve coincides very well with that observed by Barton[2] but none of the upward breaks observed by him beyond this point were found, probably because the present work was carried out at much lower pressures.

It is believed that work of this nature is of sufficient interest and importance to merit further investigation along the same line. It is planned, therefore, to extend the experiments during the next year to other gases and vapors in an attempt to gain further information on the mechanism of ionization by electron impact.

The author is ever grateful to Professor John T. Tate for his keen interest and helpful guidance during the course of this work.