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Multiple Ionization in Argon and Krypton by Electron Impact

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The formation of multiply charged ions by electron impact in argon and krypton is studied with a mass spectrometer. The behavior of the ionization cross section as a function of electron energy is investigated for electron energies up to 600 ev. The ionization potentials in ev are determined to be as follows: Kr^{2+} 38.45±0.1, Kr^{3+} 75.6±0.5, Kr^{4+} 146.6±2, Kr^{5+} 217.5±10, Kr^{6+} 350±10, Ar^{2+} 43.4±0.3, Ar^{3+} 84.8±0.5, Ar^{4+} 150.0±5. The shapes of the ionization curves near threshold are studied and discussed in terms of the threshold law for ionization. The maximum cross sections for each multiply charged ion is determined relative to that of the singly charged ion and compared to data obtained by previous investigators.

INTRODUCTION

THE studies of multiple ionization in helium and xenon by electron impact have been reported previously.[1] The work reported here is a continuation of those studies on argon and krypton. The studies were made with a 90° sectored field mass spectrometer capable of utilizing the retarding potential difference method (RPD)[2] for obtaining ionization by essentially monoenergetic electrons. The experimental procedures were the same as those reported for helium and xenon. Focusing for the ions was obtained by varying either the accelerating voltages, or the magnetic field, or both. The ion current as a function of electron energy was observed for the different ions. It was possible to make measurements for electron energies up to 800 ev.

It is apparent that instrumental effects are very difficult to eliminate from ionization probability curves taken with a mass spectrometer. It is felt that some of the points raised in this paper need further investigation. Since, however, there is no forseeable opportunity to continue these investigations and in view of the interest expressed in the obtained data, a decision was reached to submit this work for publication.

EXPERIMENTAL RESULTS

1. Krypton

The ionization curves for Kr^+, Kr^{2+}, and Kr^{3+} were obtained by using the RPD method with monoenergetic electrons. The Kr^{4+}, Kr^{5+}, and Kr^{6+} curves were obtained with the conventional electron energy spread.

The ion current near the ionization threshold for Kr^+ and for Kr^{2+} is shown in Fig. 1. The ionization for Kr^+ is observed to follow a linear threshold law. The break in the Kr^+ curve occurs at 0.6 ev above threshold, marking the onset of ionization to the $^2P_{\frac{1}{2}}$ state of the ion. The amount of tailing at the threshold is an indication of the energy spread of the electron beam. The

study of this curve has been reported previously[3] in greater detail and is reported here merely to indicate the magnitude of the electron energy distribution.

Curve b in Fig. 1 is the ionization obtained for Kr^{2+}. The energy scale has been determined, as for all the krypton multiply charged ions, from the comparison of the Kr^+ appearance potential to the ionization potential obtained from spectroscopic data. The data do not appear to follow a simple power law.[4] There is an apparent linear onset followed by two shallow maxima on an ascending curve. The upper portion of the curve has been fitted by two linear segments though the break is an indefinite one. There are four points, however, in each portion to determine the linear segments. The spectroscopically determined energy levels are indicated by the arrows. There is reasonably good agreement between the breaks in the curve and the spectroscopic energy levels with the exception of $^1D_2$ state. In this region, however, there is considerable structure which does not appear to be instrumental in origin. Possibly this is indicative of autoionization in this region.

It has been proposed from theoretical considerations[5] that near threshold the ionization should follow the law $I_+=CE^n$ where C is a constant of proportionality, E is the electron energy in excess of the ionization energy, and n is the degree of ionization. On the basis of this consideration, the data for Kr^{2+} has been replotted in Fig. 2 where $[I(Kr^{2+})]^{\frac{1}{2}}$ has been plotted vs the electron energy. The points should fit a straight line which extrapolates to the ionization potential. Except for the departure in the 40–41 ev region, the points lie on a straight line. This line, however, extrapolates to an ionization potential of 37.86 ev which is not in good agreement with the spectroscopic value of 38.56. Since the Kr^+ data was used to correct the energy scale it is difficult to understand how the energy scale can be in error by more than 0.1 ev. On the other hand, the plot of the ion current (I_+) vs the electron energy in Fig. 1(b)

[1] R. E. Fox, *Advances in Mass Spectrometry*, edited by S. D. Waldron (Pergamon Press, London, 1959), p. 397 ff.

[2] R. E. Fox, W. M. Hickam, D. J. Grove, and T. Kjeldaas, Rev. Sci. Instr. **26**, 1101 (1955).

[3] R. E. Fox, W. M. Hickam, and T. Kjeldaas, Phys. Rev. **89**, 555 (1953).

[4] This curve is in reasonably good agreement with a previously published curve by Hickam, Fox, and Kjeldaas, Phys. Rev. **96**, 63 (1954) in which the data points were made to fit linear segments intersecting at the spectroscopic energy levels.

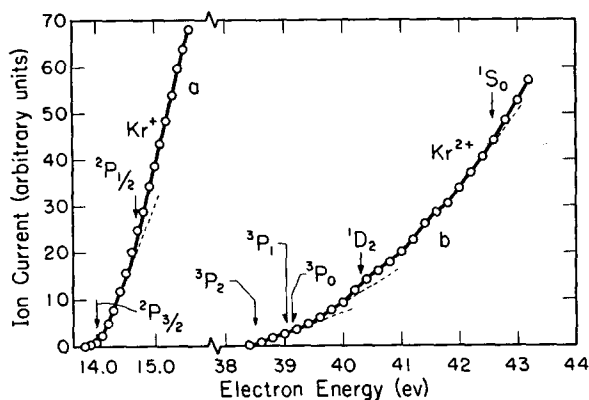[5] S. Geltman, Phys. Rev. **102**, 171 (1956).

FIG. 1. Ionization by the RPD method near threshold for (a) Kr$^+$ and (b) Kr^{2+}. The electron energy scale was determined by correcting the Kr$^+$ appearance potential to the spectroscopically determined ionization potential. The arrows indicate the excited states of the ions determined spectroscopically.

yields a value of 38.48 ev for the ionization potential in satisfactory agreement with the spectroscopic value.

The data for Kr^{3+} is shown in Fig. 3. Curve 1 shows the ion current $I(\text{Kr}^{3+})$ plotted as a function of the electron energy. The energy scale has been corrected from the Kr$^+$ data. Here linear segments have been used to fit the data and yield an ionization potential of 75.5 ev in excellent agreement with the spectroscopic value of 75.46 ev. The linear plot of Kr^{3+} (curve 1) exhibits a break at 80 ev and a second break at about 84 ev. It is not possible to correlate these breaks with any known energy states of the ion. In curve 3 the cube root of the ionization $[I(\text{Kr}^{3+})]^{\frac{1}{3}}$ has been plotted in accordance with the theory. The linear extrapolation of the straight line fit to the data points yields the low value of 71.8 ev for the ionization potential. In curve 2 the square root of the ionization $[I(\text{Kr}^{3+})]^{\frac{1}{2}}$ has been plotted as a function of the energy. The data also fits a straight line in the initial portion but yields an ionization potential of 73.5 ev.
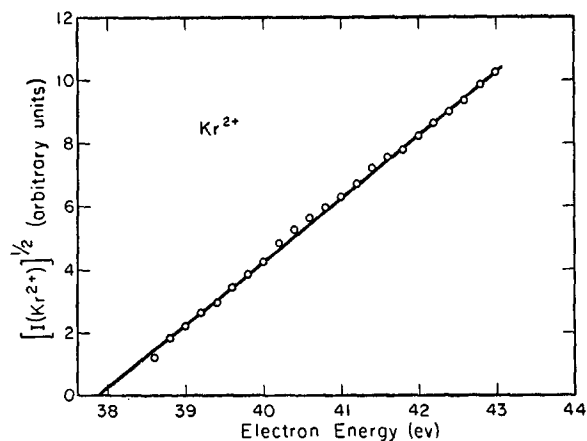

FIG. 3. Curve 1, $I(\text{Kr}^{3+})$ is plotted as a function of electron energy; curve 2, the square root of the ion current is plotted vs electron energy; curve 3, the cube root of the ion current is plotted vs electron energy. The extrapolations of the straight lines fitted to the square and cube root plots do not yield the spectroscopic ionization potential indicated by the arrow. The energy scale was determined by a slight correction of the Kr$^+$ data to fit the spectroscopic data. The data was obtained by the RPD method.

In Fig. 4 are shown the initial portions of the ionization curves for Kr^{4+}, Kr^{5+}, and Kr^{6+}. These curves were taken without using the RPD method. It is not possible to fit these data with straight lines by plotting the data as $[I(\text{Kr}^{n+})]^{1/n}$ where n is the appropriate degree of ionization.

The ionization potentials for the ions of krypton are summarized in Table I. The values shown are the averages of two runs and the errors assigned are a little larger than the differences obtained from the two values. There is good agreement between the values obtained in this work and the earlier work of Tate and Smith,[6] as well as with the values obtained from spectro-

FIG. 2. $[I(\text{Kr}^{2+})]^{\frac{1}{2}}$ is plotted as a function of electron energy. The straight line fit to the data points does not yield the spectroscopic ionization potential of 38.56 ev.
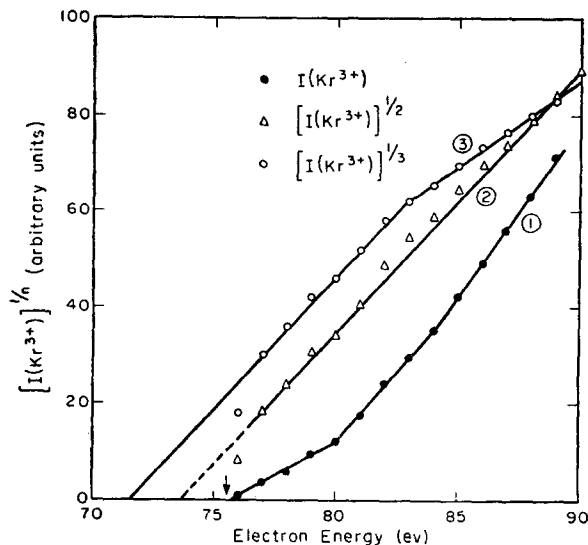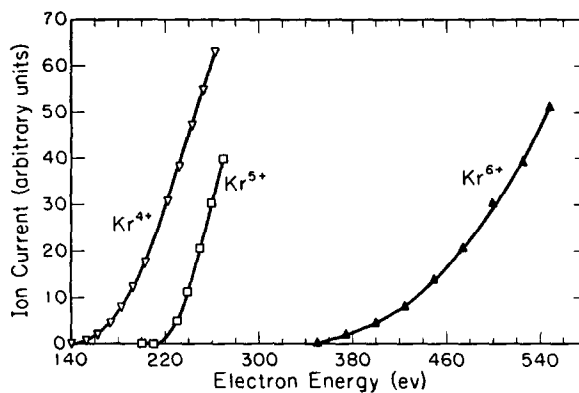

FIG. 4. Threshold ionization as a function of electron energy for Kr^{4+}, Kr^{5+}, and Kr^{6+}. The RPD method was not employed.

[6] J. T. Tate and P. T. Smith, Phys. Rev. 46, 773 (1934).

TABLE I. Ionization potentials for krypton and argon.

	Present investigator	Previous investigator	Spectroscopic
Kr$^+$	14.00[a]	13.94[b]	14.00
Kr^{2+}	38.45±.1	38.9±0.5[b] 38.6±0.2[c]	38.56
Kr^{3+}	75.6±.5	77.4±2[b]	75.46
Kr^{4+}	147±2	145±5[b]	...
Kr^{5+}	218±10	...	...
Kr^{6+}	350±10	...	...
Ar$^+$	15.76[a]	15.8	15.76
Ar^{2+}	43.4±0.3	44.1±0.5[d] 43.6±0.2[c]	43.38
Ar^{3+}	84.8±0.5	88.4±1[d] 83.7±0.5[e]	84.28
Ar^{4+}	150.0±5	259±3[d]	144.07

[a] Used as standard to calibrate energy scale.
[b] Tate and Smith.[4]
[c] Dibeler, Mohler, and Reese, J. Research Natl. Bur. Standards **38**, 617 (1947).
[d] W. Bleakney.[7]
[e] Dorman, Morrison, and Nicholson, J. Chem. Phys. **31**, 1335 (1959).

scopic data.[7] A value of about 143.5 ev for Kr^{4+} is listed by Herzberg.[8] Moore[7] does not list a value for this ion and states that the spectrum has not been sufficiently analyzed.

The ionization curves for the ions of krypton for electron energies up to 600 ev are shown in Fig. 5. All curves with the exception of Kr^{5+} and Kr^{6+} have been normalized to 100 at their maximum cross sections. The
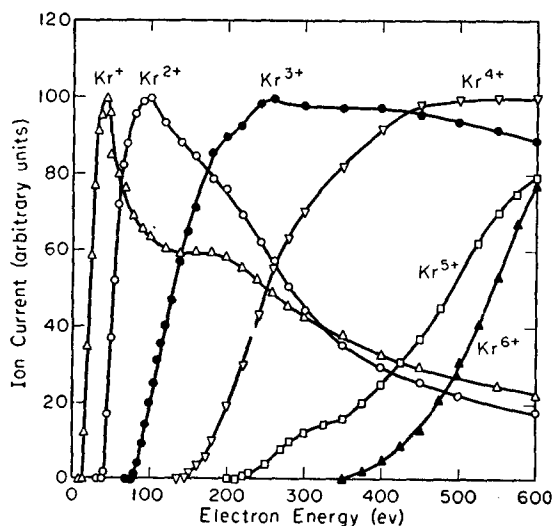

FIG. 5. The ionization for multiply charged krypton ions as a function of electron energy for a 600-ev energy range. All curves except Kr^{6+} were normalized to the same maximum ion current. Kr^{6+} was normalized to the same value as Kr^{5+} at 600 ev.

[7] C. E. Moore, *Atomic Energy Levels*, Natl. Bur. Standards Circ. No. **467**, Vol. 2 (1952).

[8] G. Herzberg, *Atomic Spectra and Atomic Structure* (Dover Publications, New York, 1944).
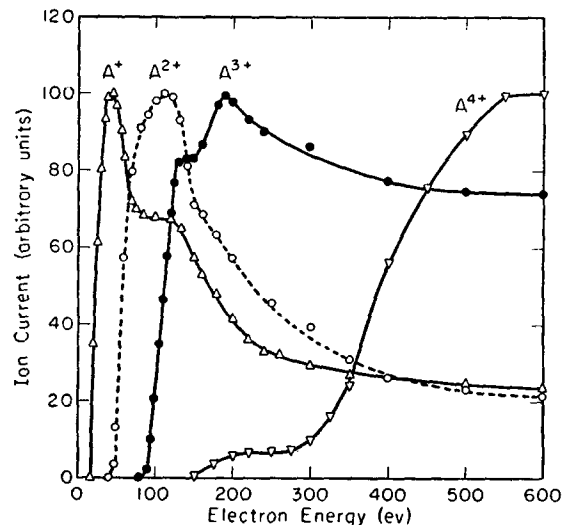

FIG. 6. Ionization curves for Ar$^+$, Ar^{2+}, Ar^{3+}, and Ar^{4+} as a function of electron energy over a 600-ev energy range. The curves were normalized to have the same maximum intensity.

relative magnitudes at the maxima are listed in Table II. It was not possible to reach the maximum cross section for Kr $^{6+}$. This curve was normalized to have the same magnitude as Kr^{5+} at 600 ev.

The over-all shape of the curves remained constant when the ions were focused either by changing the magnetic field or the ion-accelerating voltages. There was some lack of reproducibility especially at the higher energies with changing ion source parameters such as focusing electrode voltages and the auxillary magnetic field used for aligning the electron beam. The second maximum in Kr$^+$ persisted although not always with the same intensity relative to the first maximum. This shape does not agree with that obtained by Tate
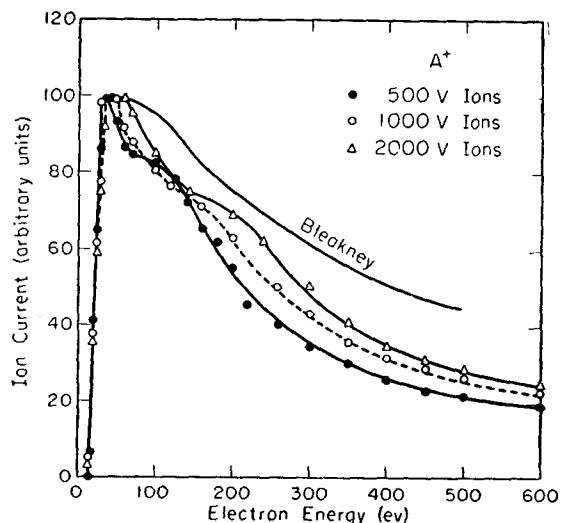

FIG. 7. Ionization of Ar$^+$ as a function of electron energy for ions having different kinetic energies. The curve with no points is that obtained by Bleakney.

and Smith, their data showing no evidence of the second maximum. This second maximum was also observed in the Xe^+ curve reported earlier.[1]

2. Argon

Ionization curves for argon taken without the RPD method are shown in Fig. 6. It is noted that the Ar^+ curve exhibits the same general shape as the Kr^+ and Xe^+ curve. If these secondary maxima are due to instrumental effects such as changes in collection efficiency of the ion source, it is difficult to understand why this effect should not be evident for all the ions observed in the same energy range.

Some of the difficulty in obtaining meaningful data with a mass spectrometer is illustrated in Fig. 7. Here is shown the ionization curve for Ar^+ for three different ion energies obtained by keeping the conditions in the

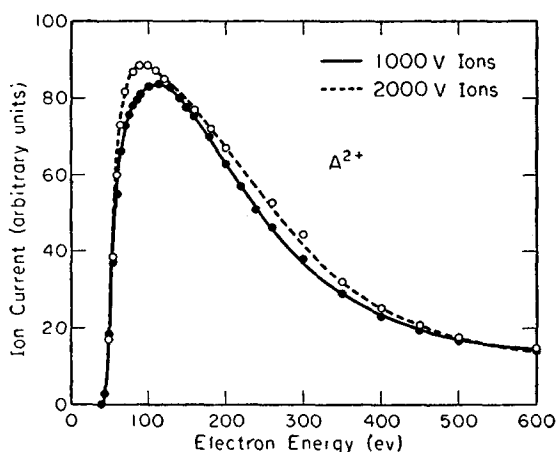FIG. 8. Ionization of Ar^{2+} as a function of electron energy for ions having different kinetic energies.

ion source constant, with the possible exception of changes in the stray magnetic field from the main magnet resulting from changes demanded by different ion-accelerating voltages, in order to refocus the ion. This effect, however, is small since magnetic shielding between the ion source and the main magnet reduces this stray field to a small amount. It is seen that there are considerable changes in the shape of ionization curves. The curves have been normalized to have the same maxima. Not only does the first maximum shift in energy but the shape of the curve from 75 to 200 ev undergoes considerable change. The shape of the Ar^+ curve does not agree with that observed by Bleakney.[9] Not only is the structure at about 100 ev energy different in the two experiments, but the amplitude decreases much more rapidly in the present experiment than that observed by Bleakney. For example, at 250 ev the Ar^+ current observed by Bleakney is 70%. This change was not as pronounced in the curve for Ar^{2+},
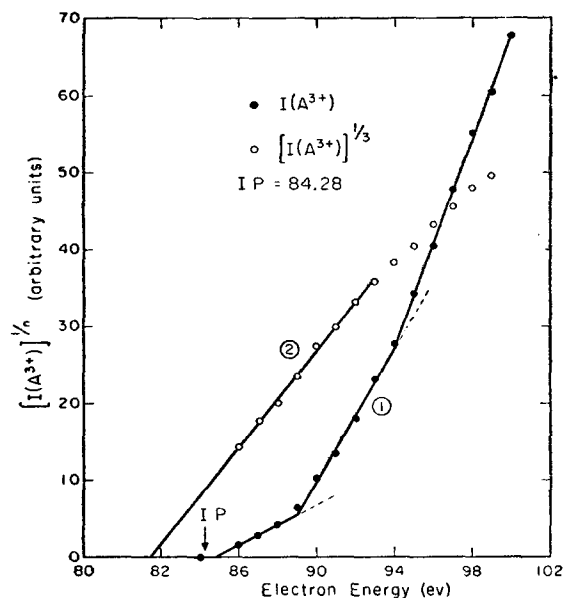
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[9] Walter Bleakney, Phys. Rev. **36**, 1303 (1950).

FIG. 9. Curve 1, the ionization of Ar^{3+} as a function of electron energy. The cube root of the ion current is plotted in curve 2. The straight line fit to the data points in curve 2 does not yield the spectroscopic ionization potential designated by the arrow.

shown in Fig. 8, although there seems to be a slight energy shift in the position of the maximum.

The ionization of Ar^{3+} near the threshold, taken with the RPD method, is shown in Fig. 9. Curve 1 shows the ion current plotted as a function of electron energy. The energy scale has been corrected from a comparison of the observed ionization potential of Ar^+ to the spectroscopically determined ionization potential. In this curve the data have been fitted with linear segments and yield an ionization potential of 84.6 ev as compared to the spectroscopic value of 84.28 ev. Curve 2 shows the cube root of the ion current plotted vs the electron energy. The straight line fit through
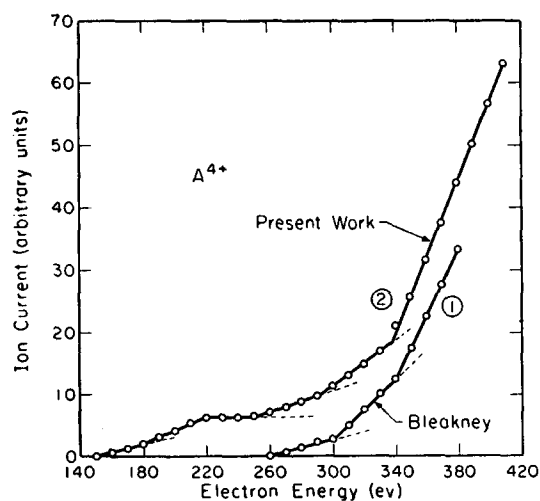

FIG. 10. The ionization of Ar^{4+} as a function of electron energy. Curve 1 shows previous results by Bleakney. Curve 2 shows present results obtained with increased detector sensitivity.

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TABLE II. A comparison of the maximum ionization probabilities for multiply charged ions of Xe, Kr, and Ar.

Ion	This work $E_{\sigma max}$ ev	Relative max ion intensity σ_{max} (arbitrary units) With multiplier	Relative max ion intensity σ_{max} (arbitrary units) No multiplier[a]	Previous work $E_{\sigma max}$ ev	Previous work Relative[a] σ_{max} (arbitrary units)
Kr^+	45	1.00	1.00	50	1.00[b]
Kr^{2+}	100	0.21	0.095	90	0.13[b]
Kr^{3+}	250	0.06	0.012	~300	0.017[b]
Kr^{4+}	550	0.008	0.0005	...	0.0018[b]
Kr^{5+}	~780	0.001	...	...	...
Ar^+	50	1.00	1.00	50	1.00
Ar^{2+}	110	0.17	0.07	120	0.10[c] 0.11[d]
Ar^{3+}	190	0.007	0.001	~200	0.005[c]
Ar^{4+}	~600	0.0008	0.00009	...	0.0007[c]
Xe^+	35	1.00[e]	1.00		1.00[b]
Xe^{2+}	60 (115)	0.40[e]	0.18		0.16[b]
Xe^{3+}	135	0.17[e]	0.05		0.05[b]
Xe^{4+}	230	0.06[e]	0.009		0.01[b]
Xe^{5+}	360	0.02[e]	0.003		0.004[b]
Xe^{6+}	~600	0.002[e]	0.00015		
Xe^{7+}	>600	0.0002[e]			

[a] These values are obtained by dividing the current ratios by the appropriate number of charges.
[b] Tate and Smith.[6]
[c] Bleakney.[9]
[d] Stevenson and Hipple.[10]
[e] Fox.[1]

the initial points extrapolates to an ionization potential of 81.5 ev which is not in agreement with the spectroscopic value.

A list of the ionization potentials for argon is given in Table I, where the values are the averages of two determinations with the exception of Ar^{4+} which is based on a single determination.

A very interesting comparison of the Ar^{4+} curve is shown in Fig. 10. The curve obtained by Bleakney[9] is shown yielding an ionization potential of 258 ev. In the present experiment the first runs obtained showed a remarkable agreement with Bleakney's curve with the exception that there seemed to be a small constant background below 260 v. The sensitivity of the ion detector was increased by about a factor of 10 by the use of an electron multiplier. The resulting curve obtained is shown in curve 2. It is seen that the curve agrees very well with Bleakney's curve above 260 ev. The curve, however, levels off to a constant value down to about 220 ev, whereupon the curve again decreases and goes to zero at about 150 ev. This value is in reasonable good agreement with the spectroscopic value of 144 ev. It is apparent that the Ar^{4+} is due to at least two processes; the first has an onset at about 150 ev and the second at about 260 ev. Bleakney apparently did not have sufficient sensitivity to observe the first process or else it was considered as a background. There is the possibility that this first process may be due to a Ne^{2+} impurity although the onset appears at the wrong energy.

The ionization curves for krypton and argon were observed with and without an electron multiplier as

the ion detector. The relative magnitudes of the maximum cross section obtained in each case are listed in Table II along with data of previous investigators.[6,9,10] $E_{\sigma max}$ designates the electron energy at which the maximum cross section occurs. σ_{max} designates the maximum cross section referred to that of the singly charged ion.

Also included in Table II are the relative cross sections of the multiply charged ions of xenon taken without a multiplier. The data taken with the multiplier have been previously reported.[1]

For the data taken without the multiplier, the ions strike the collector with essentially zero energy (<3ev) since both the ion source and ion collector are at ground potential. For the data taken with the multiplier the energy of the ions striking the first dynode depends upon the ionic charge since the potential of the first dynode is held constant with respect to the ion source. The differences in the two cases would presumably be due to the dependence of the secondary electron coefficient as a function of kinetic energy and charge. Since the first dynode was 3000 ev above ground, the energy of the singly charged ions striking the first dynode was 3000 ev.

DISCUSSION

The ionization probability curves for multiply charged ions have yielded conflicting results which are not readily resolved. These data on Kr and Ar, as well as previous data on Xe^1 obtained with the use of monoenergetic electrons, indicate that linear threshold

[10] D. P. Stevenson and J. A. Hipple, Phys. Rev. **62**, 237 (1942).

law fits the observed data better than the appropriate higher-power law predicted from theoretical considerations. Recent experiments by Krauss, Reese, and Diebeler[11] and by Morrison et al.[12] on the multiply charged ions of the rare gases produce results which are in apparent agreement with the theory.[3] However, in both these experiments the electron beam possessed a very large energy spread (~ 2 ev) although it is not clear why this should be important at these energies. It is seen from Figs. 2, 3, and 9 that the appropriate root of the ion current plotted against the electron energy can be made to fit a linear curve. These curves however, do not yield the proper appearance potentials. This effect which is also evident from the data of Morrison et al.,[12] has also been observed by Diebeler et al.

The shapes of the ionization probability curves over large energy ranges (600 ev) appear to be open to some question since some of the observed structure can be changed by changing ion source parameters. It must be remembered that the electron beam passes through several slits which are immersed in a magnetic field parallel to the axis of the slits. In changing the energy of the electrons over an appreciable range, the focal lengths of the electrostatic lenses formed by the slits change. There is undoubtedly some change in the size and/or possible spatial position of the electron beam in the ionization chamber. It is not easy to determine the extent that this effect might have on the collection efficiency of the slit system for the ions.

[11] Krauss, Reese, and Diebeler, J. Research Natl. Bur. Standards 63A, 201 (1959).

[12] J. D. Morrison and A. J. Nicholson, J. Chem. Phys. 31, 1320 (1959); Dorman, Morrison, and Nicholson, J. Chem. Phys. 31, 1335 (1959).

The unusual shapes of the Ar^+ curve and the Kr^+ curve did appear to persist (to a greater or smaller extent) for a large number of changes in the source parameters. It is felt that at least some of this structure is associated with the ionization processes of these ions.

The ionization potentials obtained appear to be in reasonable agreement with the spectroscopic values where they were available and, with the exception of that for Ar^{4+}, with the results of previous investigators. Figure 10 points out the reason for this on the basis of sensitivity differences. This curve indicates the possibility that the Ar^{4+} ions, which have an onset at about 260 ev, arise from a different mechanism than those which onset at about 150 ev. Perhaps ions formed at the higher energies are produced by Auger cascading, discussed in a previous paper.[1]

It is apparent from these experiments, as well as those of other investigators, that the difficulties in determining the threshold law for multiply charged ions are not completely resolved. It is evident that additional investigations with higher precision and with a better understanding of the ion source behavior are necessary before some of the difficulties can be satisfactorily answered.

The values for the appearance potentials obtained in this work are in good agreement with those spectroscopic ionization potentials which have been determined. The values for the relative maximum ionization probabilities are in reasonably good agreement with those obtained by previous investigators. Further investigations on the shapes of ionization probability curves over large energy ranges will be necessary before the true shapes can be known with a large degree of confidence.