175-minute activity must have the same mass number as the rubidium nucleus with 18-minute half-life, we must assume the radioactive krypton isotope to be $\mathrm{Kr}^{\geq 90}$ if the rubidium activity should be due to $\mathrm{Rb}^{\geq 90}$.

ACKNOWLEDGMENTS

The author wishes to express his sincere thanks to Dean G. B. Pegram and Professor J. R. Dunning for their continued interest and helpful advice. The author also takes pleasure in acknowledging his indebtedness to Dr. W. H. Barkas, who collaborated in the measurements on arsenic; to Dr. G. N. Glasoe and Dr. J. Steigman for many helpful suggestions in connection with the preparation of the radioactive sources; and to Mr. H. Glassford for his able assistance during the course of the experiments.

SEPTEMBER 1 AND 15, 1942 PHYSICAL REVIEW VOLUME 62

Ionization of Argon and Neon by Electron Impact

D. P. STEVENSON* AND J. A. HIPPLE
Westinghouse Electric and Manufacturing Company, Research Laboratories, East Pittsburgh, Pennsylvania

(Received June 25, 1942)

The "ionization efficiency curve" for singly charged argon is found to have at least one inflection of the type first observed by E. O. Lawrence for mercury. The relative probabilities of forming singly and doubly charged argon and neon are tabulated. Careful examination of the initial portions of the "ionization efficiency curves" for singly charged neon and argon and doubly charged argon shows the "tails" to be largely characteristic of the ionization cross section and not purely caused by spread in electron energy as often has been assumed.

THE ionization efficiency curves of the rare gases, particularly argon, are very commonly used to calibrate electron acceleration voltage scales in mass spectroscopic studies. Despite this, the form of these curves has not been extensively studied. The most complete reports on the ionization of the rare gases by electron impact are in the important papers of P. T. Smith[1] and W. Bleakney.[2] The former studied the total ionization cross sections of helium, neon, and argon as a function of the impacting electron energy. Bleakney determined the relative probability of forming singly and multiply charged ions.

In the course of checking the behavior of our 180° mass spectrometer tube we have obtained considerable data on the ionization efficiency curves of argon II (A^+), argon III (A^{++}) and neon II (Ne^+), for electrons of less than 250-volt energy. Since our data, which we believe to be more reliable for reasons given below, differ in significant detail from the previous work, we are reporting them here.

The instrument used in this research will be described in detail elsewhere, hence only pertinent details are recorded. The 180° mass spectrometer tube (16-cm radius) with the wide slits in use has a resolving power of about 1 in 150. The tube and accessories are mounted in the cavity of a water cooled spherical solenoid. A magnetic field strength of $\sim$1000 oersteds was used. The electrons were supplied by an oxide coated, platinum cathode. The electron accelerating voltage is controlled by a wire wound potentiometer and the apparent voltage measured with calibrated voltmeter which can be read with an accuracy of ± 0.1 percent. The linear variation of the positive ion current with the pressure and the current in the electron beam showed that only primary processes were observed. The total electron emission ranged from 10 to 18μ amp. while the beam itself carried from 0.5 to 4μ amp.

In Fig. 1 we show the ionization efficiency curves of the ions A^+, A^{++}, Ne^+, and Ne^{++} for electrons of less than 225-electron volt energy. The broken lines show Bleakney's results. Al-

---

* Westinghouse Research Fellow. Now at Shell Oil Company, Emeryville, California.

[1] P. T. Smith, Phys. Rev. **36**, 1293 (1930).

[2] W. Bleakney, Phys. Rev. **36**, 1303 (1930).

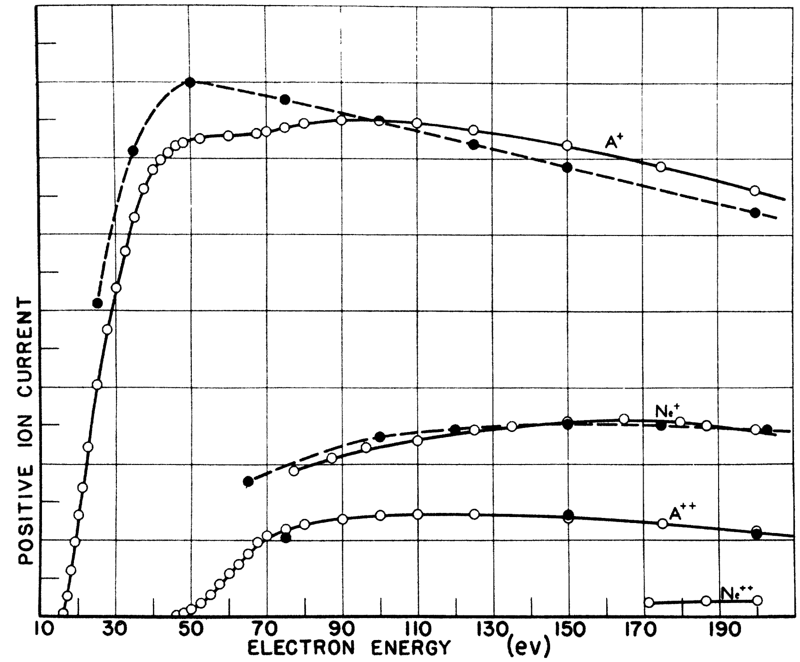

FIG. 1. The ionization efficiency curves for A^+, A^{++}, Ne^+, and Ne^{++}. Solid curves and open circles—this research. Broken curves and solid circles from reference 2 of text. The voltage scale was corrected by taking the "initial break" of the A^+ curve at 15.7 ev. The ordinates are arbitrary and different for argon and neon.

though our data for the ions Ne^+ and A^{++} are in reasonably good agreement with the earlier work, it will be noted that for $V^- > 100$ our curve for A^+ decreases more slowly than Bleakney's. Furthermore, Bleakney's curve for A^+ shows a relatively sharp maximum in the region ours shows a well-defined shoulder preceding a very flat maximum. In many respects this "peculiarity" of the ionization efficiency curve of A^+ is similar to the phenomena observed in mercury vapor.[3] Smith[1] observed the inflection in the argon ionization cross section curve at ~50 volts, but attributed it to the onset of the reaction giving A^{++}. The reason Bleakney did not observe the phenomenon probably lies in the lower sensitivity of his mass spectrometer and his use of a tungsten filament as an electron source. The much greater spread in energy of the electrons from the very hot tungsten source smears out the finer details. Even the energy spread in electrons from an oxide coated filament causes detail to be lost. This may be seen from comparison of our results on the initial portions of the ionization efficiency curve of mercury, Fig. 2, with the results of Nottingham's extremely careful study of this atom (see refer-

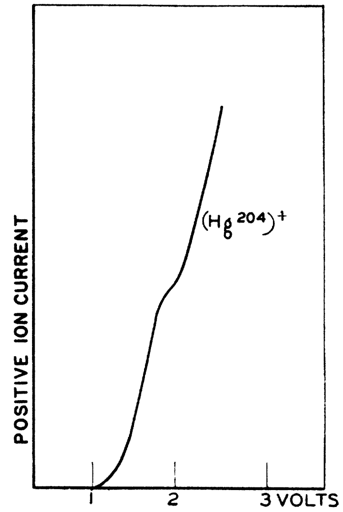

FIG. 2. The initial portion of the ionization efficiency curve for $(Hg^{204})^+$. The voltage scale is uncorrected, the ordinate arbitrary.

---

[3] a. E. O. Lawrence, Phys. Rev. **28**, 947 (1926); b. M. Bell, Phys. Rev. **55**, 201 (1939); c. W. B. Nottingham, Phys. Rev. **55**, 203 (1939).

ence 3c, Fig. 13). A careful study of argon, employing the precautions Nottingham observed, would probably reveal interesting details that our instrument is not capable of showing.

Because of their possible value for comparison with theoretical calculations we have recorded in Table I the ratios of the currents of doubly charged ions to singly charged ions for argon and neon at some round values of the impacting electron energy. The precision of the measurements, as indicated by the reproducibility, is at worst 2 percent.

Knowledge of the manner in which the ionization probability goes to zero when the electron energy approaches the ionization potential is important if ionization efficiency curves are to be used to determine critical potentials. Early workers assumed the deviations from linearity at low electron energies to be due to the spread in the electron energies.[1] Thus to obtain critical potentials the linear portion of the ionization efficiency curve was extrapolated to zero current. Tate, Smith, and Vaughan[4] in determining the ionization potential of nitrogen assumed that the ionization probability goes to zero with a finite slope but discarded the assumption of a linear dependence of the probability on electron energy. In their work on acetylene,[4] however, linear extrapolations were used to fix appearance potentials.

The approximations necessary to make quantum mechanical calculations of the ionization cross sections possible break down so badly near the critical potentials that the theory is unable to discuss the form of the initial portions of the curve. If the "tails" are primarily due to a spread of the electron energies, one would expect very close similarity to exist between the initial portions of the curves for singly charged argon and neon. The initial portions of the ionization efficiency curves of A^+ and Ne^+ are shown in Fig. 3. The ordinates for the two curves were so chosen that the linear portions are parallel. It will be noted that the tail of the curve for A^+ is considerably broader than that for Ne^+. The difference between the extrapolated linear intercepts is $5.4_7 \pm 0.1$ ev compared with the difference between the spectroscopically determined ionization potentials, 5.78 volts. These observations can be interpreted only as indicating that the curved tails are to a large extent a characteristic of the ionization process. The slope of the curve for double ionization of argon continues to increase for about 10 ev after the ion A^{++} first appears. This is to be compared to the 1- to $2\frac{1}{2}$-volt region in which the slope of the curves for A^+ and Ne^+ increases.

TABLE I. Ratio of currents of doubly and singly charged ions.

Electron energy V^- volts	Argon $(i++/i+)$[a]		Neon $(i++/i+)$[a]	
50	0.014	(0.021)[b]		
60	0.090			
70	0.167	(0.138)		
80	0.186			
90	0.197			
100	0.204	(0.208)		(0.034)[c]
125	0.210			
150	0.208	(0.223)		(0.081)
175	0.204		0.074	
200	0.199	(0.210)	0.082	(0.114)
225	0.193			

[a] These are ratios of currents. The relative ionization probabilities are obtained by dividing the tabulated quantities by 2.

[b] Bleakney, reference 2 of text. These values were obtained from measurements made on a photographic enlargement of Fig. 6 of reference 2. From Fig. 3 of Tate, Smith, and Vaughan [Phys. Rev. **48**, 525 (1935)] one finds for $V^- = 100$ volts $A^{++}/A^+ = 0.216$.

[c] Figure 3 of reference 2.

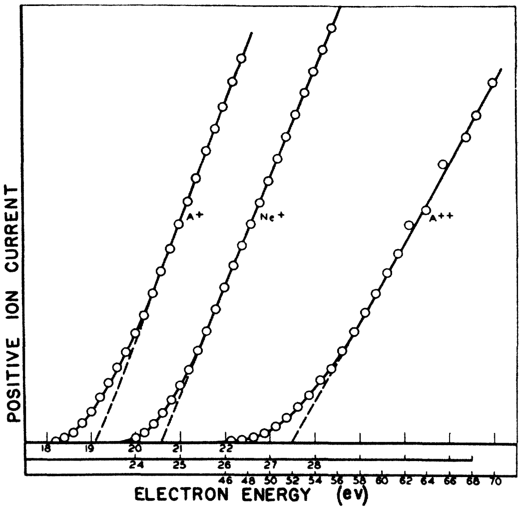

FIG. 3. The initial portions of the ionization efficiency curves for A^+, Ne^+, and A^{++}. Ordinate arbitrary and different for each curve. Note that voltage scale for A^{++} is $\frac{1}{4}$ that for A^+ and Ne^+, and that to save space the curves have been subjected to horizontal translation.

If one draws a smooth curve through the observed points and extrapolates to zero current assuming an essentially zero initial slope, the differences between the intercepts are $(Ne^+)_0 - (A^+)_0$

---

[4] J. T. Tate, Z. T. Smith, and A. L. Vaughan, Phys. Rev. **48**, 525 (1935).

$=5.6_5\pm0.15$ ev and $(A^{++})_0-(A^+)_0=28._0\pm0.5$ ev. These differences agree with the spectroscopic values[5] within the experimental uncertainty of our results. These results seem to provide real justification for determining differences between appearance potentials from the initial breaks of curves obtained under similar conditions of sensitivity.[6] This procedure clearly reduces uncertainties due to contact potentials and the spread in the electron energy by cancellation. The close check between the electron impact and spectroscopic results indicates that the difference in the sharpness of onset of ionization introduces no error as great as that inherent in the mass spectroscopic measurements themselves.

APPENDIX I

We assume that the probability of the reaction

$$X+\epsilon^-\rightarrow X^++2\epsilon^-$$

is given by the expressions,

$$\rho(V^-)=0 \qquad V^-\leqslant I^z=\text{ionization potential of } X, \tag{1}$$

$$\rho(V^-)=(V^--I^z) \qquad V^-\geqslant I^z, \tag{2}$$

where $\rho(V^-)$ is the probability of the ionization of X by an electron of energy V^-. Furthermore, we assume that the energy of the electrons in the bombarding beam is

$$V^-=V_a+\epsilon$$

where V_a = applied potential and ϵ = thermal energy, and that the distribution in ϵ is Maxwellian, i.e.,

$$n(\epsilon)=KN^-(1/kT)^{\frac{3}{2}}\epsilon^{\frac{1}{2}}e^{-\epsilon/kT}$$

where T = characteristic absolute temperature, N^- = total current in beam. Then the positive ion current as a function of the electron energy, for the parameter $\beta\geqslant0$, is

$$I^+(V_a)\propto\frac{2}{\sqrt{\pi}}\left[\tfrac{3}{2}\beta^{\frac{1}{2}}e^{-\beta}+\frac{\sqrt{\pi}}{2}(\tfrac{3}{2}-\beta)\{1-\Phi(\sqrt{\beta})\}\right] \tag{3}$$

$$\beta=(I^z-V_a)/kT$$

$$\Phi(\sqrt{\beta})=\frac{2}{\sqrt{\pi}}\int_0^{\sqrt{\beta}}\exp(-u^2)\,du,$$

TABLE II. Test of Eq. (5).

Molecule	ion	$I^+(\beta=\frac{3}{2})\div$slope
Neon	Ne^+	$0.24_3\pm0.01$
Argon	A^+	$0.33_4\pm0.01$
Argon	A^{++}	$1.5_2\pm0.1$
Ethane	$C_2H_6^+$	$0.20_6\pm0.01$
Propane	$C_3H_8^+$	$0.24_1\pm0.01$
n-butane	$C_4H_{10}^+$	$0.28_6\pm0.01$
i-butane	$C_4H_{10}^+$	$0.29_4\pm0.01$
Propylene	$C_3H_6^+$	$0.30_2\pm0.01$
iso-butylene	$C_4H_8^+$	$0.24_7\pm0.01$
Equation (5)	—	0.465

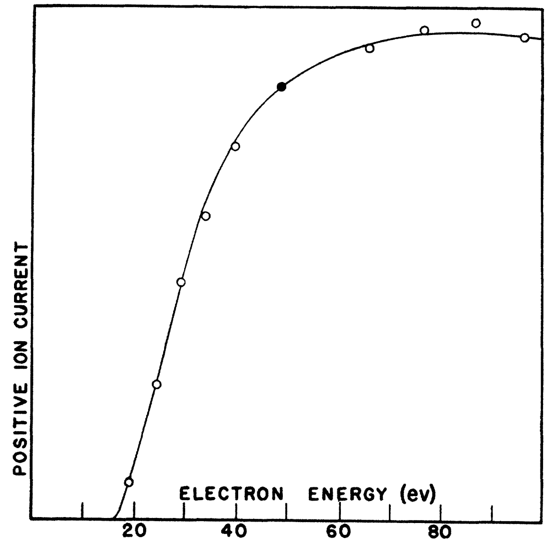

FIG. 4. The curve shows the ionization efficiency curve for N_2^+ determined by Hagstrum and Tate (reference 8). The open circles are from this research. The closed circle indicates the point at which the two curves were arbitrarily made to fit.

while for $\beta\leqslant0$

$$I^+(V_a)\propto(\tfrac{3}{2}-\beta). \tag{4}$$

The constant of proportionality is the same for Eqs. (3) and (4), thus for $\beta=\frac{3}{2}$ the positive ion current should be

$$\left[I^+(V^-)=C\cdot\frac{2}{\sqrt{\pi}}\left(\frac{3}{2}\right)^{\frac{3}{2}}e^{-\frac{3}{2}}\right]=0.465\ C, \tag{5}$$

where C is the proportionality constant or the slope of the linear portion of the ionization efficiency curve. In Table II we record the observed value of the ratio of I^+ (at linear intercept) to slope for a number of atoms and molecules.

Since the form of the energy distribution of the electrons is well established,[7] the failure of Eq. (5) to agree with the experiments indicates that Eq. (2) is without justification.

APPENDIX II

As a check on the reliability of the ionization efficiency curves of Fig. 1 as plotted from data taken with our instrument, our curve for N_2^+ was compared with that reported by Hagstrum and Tate;[8] Fig. 4 shows the very satisfactory agreement of these curves and tends to promote confidence that the inflection in the A^+ curve is real. Another favorable factor is the excellent agreement obtained for the ethane spectrum taken with this instrument and the crossed-field instrument at Princeton.[9]

---

[5] R. F. Bacher and S. Goudsmit, *Atomic Energy States* (McGraw-Hill, New York, 1932). I^z(A I) = 15.69 volts. I^z(A II) = 27.72 volts. I^z(Ne I) = 21.47 volts.

[6] L. G. Smith, Phys. Rev. **51**, 263 (1937) and reference 4.

[7] K. T. Compton and I. Langmuir, Rev. Mod. Phys. **2**, 123 (1930).

[8] H. D. Hagstrum and J. T. Tate, Phys. Rev. **59**, 354 (1941).

[9] D. P. Stevenson and J. A. Hipple, J. Am. Chem. Soc. (to be published).