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PROBABILITY AND CRITICAL POTENTIALS FOR THE FORMATION OF MULTIPLY CHARGED IONS IN HG VAPOR BY ELECTRON IMPACT

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Abstract

With a type of apparatus previously reported the procedure is described for measuring the probability of the formation of multiply charged ions in mercury vapor as a function of the velocity of the incident electron.

Critical potentials for the formation of multiply charged ions. New results together with those of an earlier paper place the minimum or ionizing potentials for the formation of Hg^+, Hg^{2+}, Hg^{3+}, H^{4+}, and Hg^{5+} by a single impact at 10.4, 30, 71, 143, and 225 volts respectively. A brief correlation of these results with those of other observers is given.

Relative numbers of multiply charged ions. A set of curves is given showing the fraction of the total positive ion current carried by each type of ion as a function of the electron velocity. Another set of curves shows the fraction of the total number of ions carrying one, two, three, four, and five charges. The fraction for Hg^+ drops to a nearly constant value of 78 percent while the value for Hg^{2+} approaches 16 percent of the total number beyond 150 volts. At 400 volts the values for the five ions in order are 77, 16.5, 4.4, 1.3 and 0.8 percent respectively.

Quantitative measure of the number of ions produced and effective cross-sectional area of the Hg atom. Curves are given representing the number, N, of each type of ion, per electron, per cm path, per mm pressure at 0°C as a function of the electron velocity. The values of N for Hg^+, Hg^{2+}, Hg^{3+}, and Hg^{4+} have maxima of 20.8, 3.2, 0.72, 0.15 at 50, 115, 210, and 400 volts respectively. The effective cross-sectional area of the Hg atom toward an ionizing collision of a given type is obtained by dividing the appropriate value of N by the number of molecules per cc. The maximum value of this area for Hg^+ is about 60 percent of the kinetic theory value.

A discussion is given of the meaning of the area under the peaks in the e/m analysis curves and its effect on the accuracy of the interpretation of the data.

I. Introduction

BEFORE our knowledge of the probability of ionization in gases by electron impact can be complete it is necessary to investigate the critical potentials for the formation of multiply charged ions, and the effective cross-sectional area of the molecule or atom toward an ionizing collision as a function of the energy of the incident electron. Heretofore the types of apparatus used by investigators in this field have been such that the total number of unit positive charges was observed and not the actual number of ions formed since

an ion may carry several positive charages. It is important, therefore, to study separately the probability of the formation of ions having one, two, three, or more charges. Until recently no direct experimental method had been devised capable of such an investigation. The success of any method requires that only the primary products be examined, that is, the pressure of the gas must be such that there is little chance of an electron colliding twice and the current density of electrons must be so low that there is also little chance of an ion being struck a second time. The scheme proposed in a recent paper[1] lends itself very well to work of this kind. As yet a study has been made of mercury vapor only. A preliminary report[2] of some of the results has already been made.

II. Apparatus and Procedure

The apparatus used in the present experiment has already been described[1] in considerable detail and the reader is referred to this paper for the principles and details of the design. A plan view is shown in Figs. 1 and 2 for convenience in the discussions which follow.

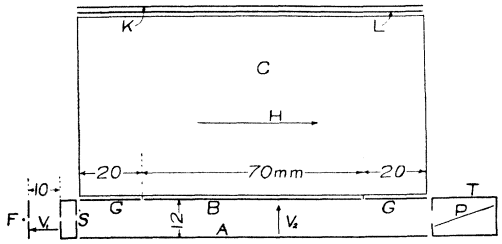

Fig. 1. Side view of apparatus.

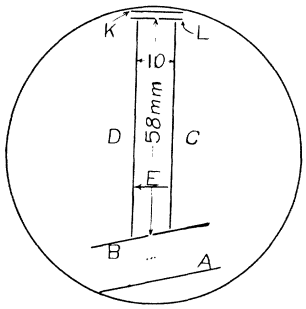

Fig. 2. End view.

The pressure of the mercury vapor was controlled by regulating the temperature of a trap in the exhaust line containing liquid mercury. The data for the pressure of the vapor corresponding to the temperatures used were taken from the International Critical Tables. The best temperature at which to work was found to be in the neighborhood of -20°C or a pressure of 1.81×10^{-5} mm Hg. Temperatures in this region were maintained either by a mixture of NaCl and ice or by solid CCl_4. The latter melts at -24°C. The temperature of the ionization chamber was measured by means of a thermocouple and was always found to be about 45°C. Since the mean free path of the atoms was much greater than the diameter of the connecting tube a pressure correction for diffusion was made to get the true pressure in the tube.

The electron current required in most cases was about 3×10^{-7} amperes. It was measured by means of a galvanometer of 4,000 megohms sensitivity. A potential (usually about 90 volts) was applied to the plate P positive with respect to the surrounding box of a magnitude sufficient to give a saturation current. The galvanometer measured the current to the box and plate com-

[1] W. Bleakney, Phys. Rev. **34**, 157 (1929).
[2] W. Bleakney, Phys. Rev. **35**, 123 (1930).

bined, thus obviating any correction due to ions being formed inside the box. It is believed that secondary electrons escaping from this arrangement were quite negligible. The positive ion current arriving at the plate B was measured with a Leeds and Northrup galvanometer of 110,000 megohms sensitivity. Saturation current to this plate was observed with a field V_2 as low as 0.3 volts per cm. The field strength used for the final runs was 3.3 volts per cm. The current to the plate K was measured with a Compton electrometer at a sensitivity of 2000 mm per volt. For the larger currents a direct deflection was observed by shunting the instrument with India ink resistances. For very small currents the time required to deflect through a given distance on the scale was measured.

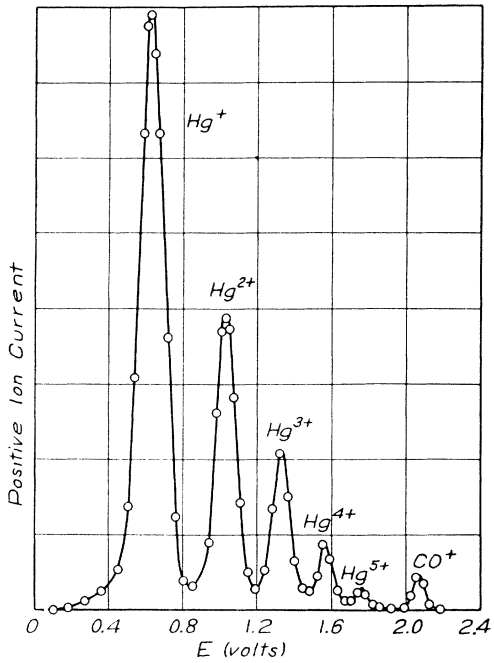

Fig. 3. A typical e/m analysis curve. $V_1 = 350$ volts. $p = 1.8 \times 10^{-5}$ mm Hg.

A set of preliminary runs was taken at various values of the field V_2. It was found that the relative sizes of the peaks remained unchanged between 1.2 and 3.5 volts per cm. A second set of preliminary runs was taken at various pressures, the results showing that the effects of scattering and neutralization were negligible at the pressures finally used. The final set of runs was then taken at electron velocities ranging from 20 to 500 volts.

III. Results

In Fig. 3 is shown a curve typical of a large number obtained with the apparatus. The electrometer current is plotted as a function of the crossed field E. In this instance the accelerating potential for the electrons V_1 was set at 350 volts, the drawing out field V_2 at 3.3 volts per cm, and the pressure was that corresponding to saturated mercury vapor at $-20°$C or 1.8×10^{-5} mm

Hg. The magnetic field furnished by the solenoid amounted to 400 gauss. The curve distinctly reveals the five mercury ions Hg^+, Hg^{2+}, Hg^{3+}, Hg^{4+}, and Hg^{5+}. Only one impurity shows up to any extent and its ionization potential was found to be 14.5 volts. It seems certain then that it is a singly charged ion and its position indicates a molecular weight of 28. These two facts are strong evidence for its being a CO^+ ion.

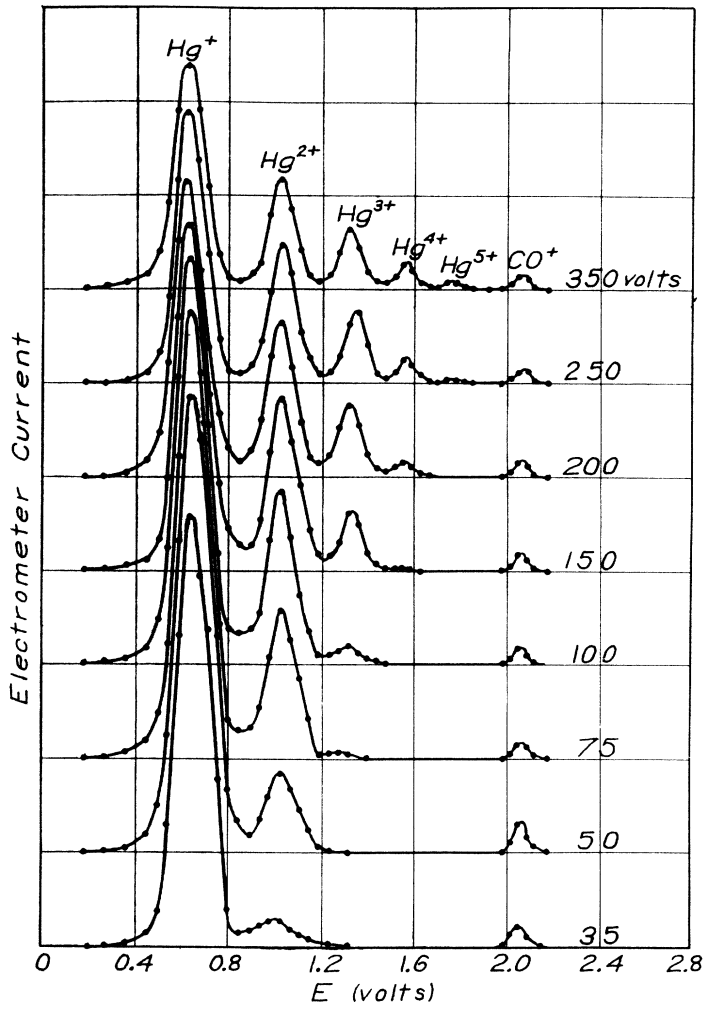

Fig. 4. A series of e/m analysis curves taken at various electron velocities.

Figure 4 illustrates a series of curves taken at electron velocities ranging from 35 to 350 volts. The ordinates of the different curves have been reduced to correspond to the same pressure and the same electron current throughout.

Critical potentials for the formation of multiply charged ions at single impact. If the areas under the peaks are plotted as a function of the electron velocity and the curves extrapolated to zero area the minimum or critical potentials for the formation of the different ions at a single collision are obtained. These

values may be called the ionization potentials for single impact. To the four values reported in the first paper[1] there is now added a fifth. The curves are shown in Fig. 5. The ionization potential for Hg^{5+} was difficult to determine with any accuracy because of the proximity of the Hg^{4+} peak and a very

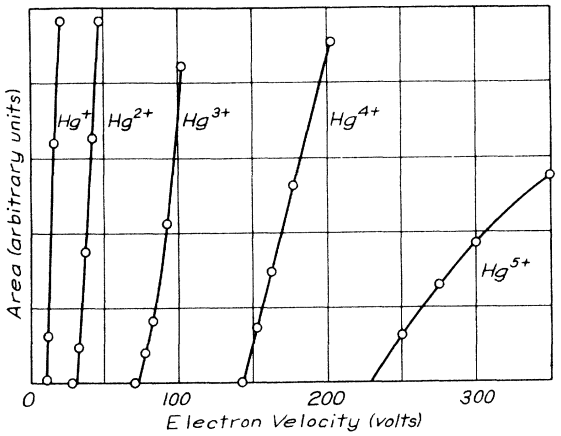

Fig. 5. Curves showing the ionization potentials at single impact.

slight impurity which coincided with the Hg^{5+} peak. Assuming the value of Hg^{+} to be 10.4 volts the values, with the estimated probable errors, of Hg^{2+}, Hg^{3+}, Hg^{4+}, and Hg^{5+} are placed at 30 ± 1, 71 ± 2, 143 ± 3, and 225 ± 5 volts respectively. There has been observed only slight evidence for the Hg^{6+} ion while Hg^{7+} and Hg^{8+}, if any are formed, are completely masked by the CO^{+} impurity.

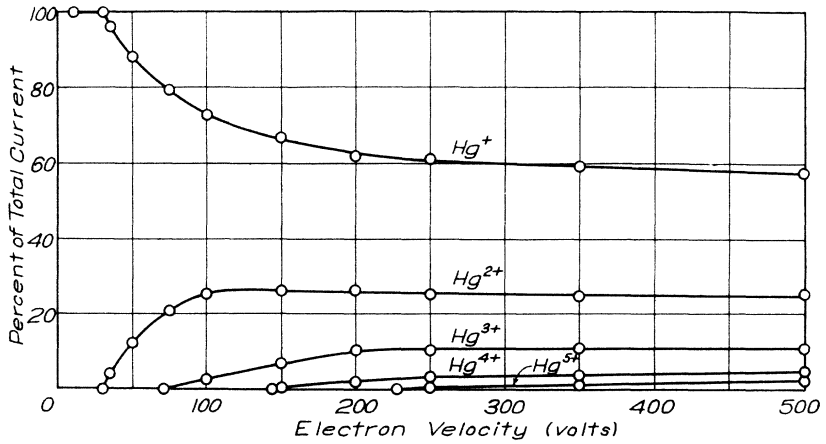

Fig. 6. Percent of total current carried by each type of ion.

Relative numbers of multiply charged ions. It will be assumed that the area under each peak of the e/m analysis curves is proportional to the current due to that particular type of ion and the validity of this assumption will be examined later. The curves of Fig. 6 representing the fractions of the total

current due to the different ions are obtained by plotting the area under each peak divided by the total area as a function of the electron velocity. Between 10.4 and 30 volts the positive ion current is 100 percent singly charged, and the effect of the appearance of the other ions is to lower this value to a nearly

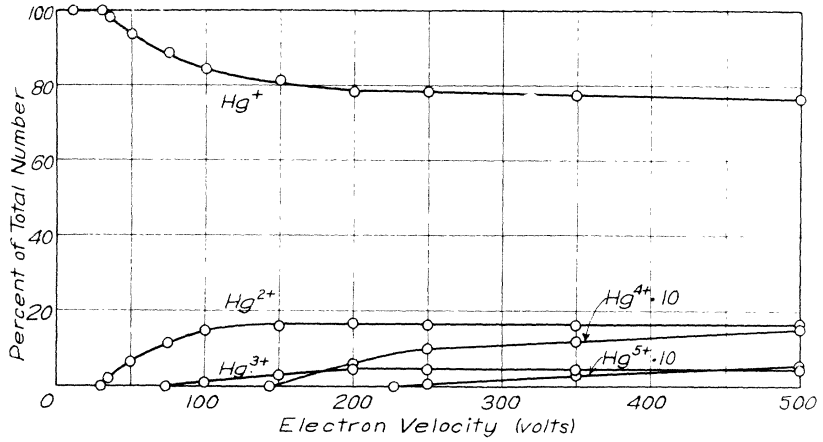

Fig. 7. Percent of total number of ions having one, two, three, four and five charges.

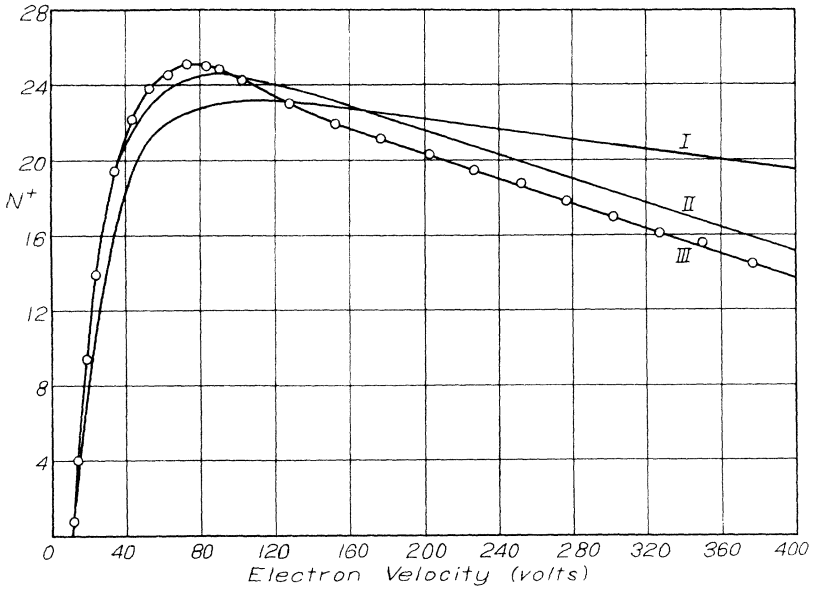

Fig. 8. Total number of positive charges, N^+, per electron per cm path per mm pressure at 0°C.

constant one of 59 percent at the higher velocities. The fractions of the total current due to Hg^{2+} and Hg^{3+} reach maximum values of 27 and 11 percent respectively.

To find the relative abundance of the different ions in *number* it is necessary to consider the total area under the first peak, one half the area under the

second, one third the area under the third, and so forth, as fractions of the sum. The curves of Fig. 7 show the results of this calculation. The ordinates for the fourth and fifth ions are here multiplied by 10. It will be noticed, for instance, that while at 300 volts the current due to Hg^+ is only 60 percent of the total yet 78 percent of the ions actually formed are singly charged.

Quantitative measure of the number of ions and the effective cross-sectional area of the Hg atom. As has been stated before the total number of positive charges arriving at the plate B was measured. Let the number of positive charges formed per electron per cm path per mm pressure at 0°C be denoted by N^+.

The values of N^+ are indicated in Fig. 8 as a function of the electron velocity. The curves of two other observers are shown for comparison. Curve I,

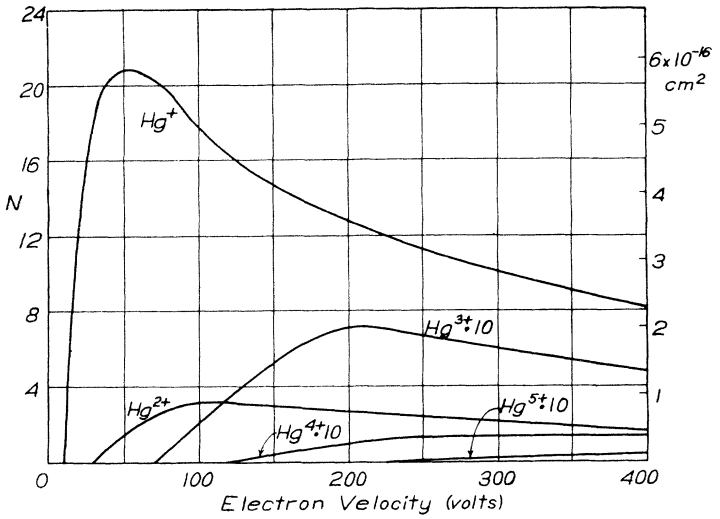

Fig. 9. Number of Hg^+, Hg^{2+}, Hg^{3+}, Hg^{4+}, and Hg^{5+} ions per electron per cm path per mm pressure at 0° C and effective cross-sectional area of the Hg atom.

reduced to 0°C, is from the work of Compton and Van Voorhis.[3] Curve II, corrected to conform to the pressure and temperature data used in this article, is taken from the paper by T. J. Jones.[4] Curve III was obtained by the author and was used in the calculations which follow. Curves II and III agree fairly well as indeed they should since they were obtained by the use of the same type of apparatus. The maximum in the curve found in the present experiment has a magnitude of 25.2 at 75 volts compared to 24.6 at 90 volts as observed by Jones. Beyond the maximum the results of Jones are consistently higher than curve III. At present an attempt is being made in this laboratory with a new apparatus to measure the quantity N^+ with greater accuracy. If such a determination should prove different from the results here given the following results may be easily revised to conform to the new data.

[3] K. T. Compton and C. C. Van Voorhis; Phys. Rev. **26,** 436 (1925) and **27,** 724 (1926).
[4] T. J. Jones, Phys. Rev. **29,** 822 (1927).

Having measured the total number of positive charges and the fraction due to each type of ion it is possible to calculate the actual number of each type by taking values from the curves of Fig. 6, multiplying by the corresponding N^+ from Fig. 8 and dividing by the number of charges on the ion. These results have been plotted in Fig. 9 where N is the number of ions per electron per cm path per mm pressure at 0°C as a function of the electron velocity. The ordinates for the last three ions have been multiplied by 10. Now if the number N be divided by the number of atoms per cc the quotient is the effective cross-sectional area of the Hg atom toward an ionizing collision. This area is indicated by the scale on the right margin of Fig. 9. The kinetic theory value for this area is in the neighborhood of 10×10^{-16} cm^2 depending on one's choice of the recorded values for the diameter of the mercury atom. Although the total positive ion current exhibits a maximum at an electron velocity of about 75 volts yet when the ions are examined separately the maximum yield for Hg^+ occurs at 50 volts. Maxima for Hg^{2+}, Hg^{3+} and Hg^{4+} appear at 115, 210, and 400 volts respectively.

IV. Discussion

Because of its complicated structure there has been no theoretical treatment worked out to predict the ionization potentials in mercury vapor. Of course the first, 10.4 volts, is well known from a host of critical potential experiments. The determination by Lawrence[5] is probably the most accurate, and his value agrees with spectroscopic measurements. Smyth,[6] using a method of positive ray analysis, found doubly charged ions appearing at 19 volts while Carroll,[7] from an analysis of the spectrum of Hg II, gets the same value. These values represent the energy necessary to remove the second electron after the first is gone. If the energy required to remove the first is included they are in satisfactory agreement with the value given by the present investigation.

It was assumed, earlier, that the area under any peak in the e/m analysis curve was proportional to the current due to that type of ion. Suppose the ions are traveling in the x direction and the slit has a width dy. Then for any particular setting of the field E the electrometer measures the number of ions which fall between y and $y+dy$ a quantity which is equivalent to dn/dy where n is the total number of charges between y_0 and y. This is the quantity which is plotted as a function of E, and measuring the area under the curve is equivalent to performing the integration,

$$\int_{E_0}^{E_1}(dn/dy)dE$$

a quantity which has dimensions different from that which we wish to find. The integral which we would like to find is

$$\int_{E_0}^{E_1}(dn/dy)(dy/dE)dE$$

[5] E. O. Lawrence, Phys. Rev. **28,** 947 (1926).
[6] H. D. Smyth, Proc. Roy. Soc. **A102,** 283 (1922).
[7] J. A. Carroll, Phil. Trans. Roy. Soc. **A225,** 365 (1925).

and only in case dy/dE is equal to a constant is the area as measured proportional to the current. The analytical expression for dy/dE can be found from the equations of motion but it is not simple and it involves the unknown initial velocity distributions of the ions. The numerical value therefore can only be roughly approximated. It was thought, therefore, that an experimental attack might prove more fruitful.

Professor Tate pointed out that if the factor by which the area under a peak must be multiplied to get the current is the same for all the peaks then this factor is equal to the total current entering the analyzing chamber divided by the total area under the curve. It was decided, therefore, to measure the current and area at various electron velocities to see if the ratio remained constant when different peaks were involved. The current issuing from the first slit was measured with the high sensitivity galvanometer while the electrometer measured the current through the second slit in the usual way. The experimental error of such a determination is rather large because of the low intensity of the current to the galvanometer. Ten runs were made with electron velocities ranging from 20 to 70 volts. Below 30 volts only the single ion is formed while below 70 volts only single and double ions may exist. In these runs the ratio of current to area showed a maximum deviation of 3 percent from the mean and displayed, moreover, no systematic variation with increasing numbers of doubly charged ions. Tests at higher electron velocities gave similar results although the experimental error was greater. The conclusion is that the area is proportional to the current within the experimental error of this test. It should be pointed out, however, that the experimental error for the determination of the ratio for the second peak alone is perhaps ten or twelve percent since it contains at most only about one fourth of the total area. In general the smaller the peak the less certain are the measurements.

Another test was made by connecting the galvanometer to the plate C Fig. 2, and measuring the current arriving at this plate as a function of the field E. With $E=0$ all the positive ions issuing from the lower slit fell upon C. As E was increased a point was reached at which singly charged ions were prevented from reaching the plate and the remainder was measured by the galvanometer. Here, also, the accuracy is not great because the separation of the ions is not precise at the current densities required, but the results agreed substantially with the previous test.

The original data as represented by the curves in Fig. 4 can be reproduced quite accurately. It is in the interpretation that great care must be exercised lest errors creep in. It is believed that the results as represented by the curves in Figs. 5 and 6 are very close to the true values.

The calculation of the probability of formation of the different types of ions is dependent on the measurements of the total ionization and different observers are somewhat at variance on these values. The results obtained in the present work are in fair agreement with those of Jones, and Compton and Van Voorhis (see Fig. 8) but are not at all in agreement with those of von

Hippel.[8] It is argued by him that a crossed field due to contact potentials swept out the multiply charged ions before they were measured and hence his results apply to Hg^+ only. Even so, the author cannot correlate von Hippel's data with the present work, and it appears that his theory that the maximum yield occurs at twice the ionization potential is untenable.

Smyth,[6] who was the first to investigate the multiply charged ions in mercury vapor by means of a mass spectrograph, states that at the higher velocities the number of doubly charged ions is nearly equal to the number singly charged. From the appearance of his curves it is probable that it is the *current* which is nearly equal in the two cases. If this be true then both Jones and von Hippel have misinterpreted Smyth's data.

It seems to be quite generally assumed that the classical kinetic theory value for the mean free path of an electron is $4(2)^{1/2}$ times the mean free path of an atom of the gas. This value has apparently been used by Hughes and Klein,[9] Compton and Van Voorhis,[3] Jones,[4] and others in their calculations. It seems to the author that this is not the true kinetic theory value for high speed electrons such as were used in all of these experiments, the more appropriate value being

$$\lambda = 1/\pi r^2 N$$

where N is the number of atoms per cc and πr^2 is the kinetic theory value of the cross-sectional area of an atom. The difference in the two points of view is very marked in the case of mercury. The maximum effective cross-sectional area of a mercury atom toward an ionizing collision of the first type calculated on the basis of the latter argument is at least 60 percent of the kinetic theory value, while Jones, and Compton and Van Voorhis on the basis of their calculations get a little over 30 percent for any type of ion. It is interesting to note in the curves of Compton and Van Voorhis that mercury vapor gives the largest yield of positive charges of any gas used and it is among the lowest in probability of being ionized and yet the kinetic theory value for the size of the mercury atom does not differ greatly from the others.

The author has been unable to check the calculations for curve 2, Fig. 3, in the paper by Jones[4] and it is believed that this curve is in error. It also seems that a correction for diffusion due to the large difference in temperature between trap and tube should have been made in the pressure before calculating the values for curve 1 of this same figure.

It is essential to point out that while the number of Hg^+ ions, for instance, has been measured yet what electron was removed in its formation is unknown. This fact makes a theoretical explanation of the observed phenomena even more difficult.

Work on hydrogen and the rare gases has been started and it is hoped that these results may be reported in the near future.

Many thanks are due Professor John T. Tate for his ever present interest and timely suggestions in the prosecution of this problem.

[8] A. v. Hippel, Ann. d. Physik **87,** 1035 (1928).

[9] A. L. Hughes and E. Klein, Phys. Rev. **23,** 450 (1924).