THE PROBABILITY LAW GOVERNING IONIZATION BY ELECTRON IMPACT IN MERCURY VAPOR

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Abstract

Despite several attempts, the unusual type of probability law found by Lawrence to govern inelastic impacts in mercury vapor just above the ionization potential, has not been verified by other observers. His experiment, making use of a magnetic separation of the electron beam and a Faraday cylinder type of ionization chamber, has been criticized on the basis that electron reflection from the walls and other spurious wall effects might account for the results. Since no theory has predicted such a probability law it seemed important that a new investigation be launched in an attempt to prove or disprove its validity. An apparatus providing an electron beam approaching in homogeneity that of the Maxwellian distribution should make such a test readily possible. An electron-gun type of ionization tube was devised, capable of high resolving power, and eliminating the objectionable features of the Lawrence method. Using a dull emitter cathode it was found possible to approach very closely the theoretical Maxwellian velocity distribution. With this arrangement the new critical potentials of Lawrence were checked and his probability law verified within the limits of experimental error. The values of these critical potentials are: 10.6; 11.3; 11.7; and 12.1 volts. Additional ionization potentials at 12.3; 12.45; 12.85; and 13.2 volts were also found. A search for critical potentials above 13.2 volts yielded negative results. The results indicate that the failure of other experimenters to detect this probability law was due to their wide distribution of electron velocities. Since this is true, the values which they have given for the probability of ionization in this region can be considered as correct only in order of magnitude. Evidence is presented to show that these critical potentials are a result of the ionization of metastable mercury atoms, the probability law indicating either a high concentration of such excited atoms, or a large collision cross section for a metastable atom toward an ionizing collision. Data concerned with the variation of ionization current with electron current density, seem to favor such an hypothesis but is not decisive in character. When mercury vapor is admitted to the tube, the widening of the velocity distribution indicates the existence of a new type of atomic collision process. In this process the electrons lose energies of only a small fraction of a volt. These low energy losses are now being investigated together with additional evidence concerning the metastable atom hypothesis.

Introduction

The form of the probability law governing ionization in the region just above the minimum ionization potential was first subjected to close scrutiny by Lawrence.[1] His work indicated, first, the existence of several new critical potentials for inelastic impact, lying just above the minimum ionization potential, and, second, that the probability of ionization in this range was not a continuous monotonically rising function of the electron energy as had been concluded from the results of other investigations.[2,3,4,5,6] In fact,

[1] E. O. Lawrence, Phys. Rev. **28**, 947 (1926).

[2] A. L. Hughes and E. Klein, Phys. Rev. **23**, 111 (1924); **23**, 450 (1924).

the probability of ionization was not zero at the minimum ionization potential but had a finite value, which, with increase in electron energy, decreased to a point where it took on a sudden increment at the next critical potential. There was then a further decrease with a second subsequent increment, etc.

Later these so-called ultraionization potentials were again observed by Lawrence[7] and also by Morris,[5] and by Hughes and Van Atta[8] using the ordinary total current methods, but no evidence of the peculiar type of probability law, earlier found by Lawrence, was obtained. In fact, Morris concluded from the results of his experiment, that the probability law of Lawrence must be in error and offered the alternative hypothesis that the probability of ionization was proportional to the excess of energy of the electron over the amount required to produce a given ultrastate.

The purpose of this investigation was to see whether the existence of a probability law of the type proposed by Lawrence could be verified without using his technique of magnetic separation. This was important, since, as von Hippel[9] pointed out, the Lawrence method permits the possibility of an explanation of any new critical potentials on the basis of spurious effects, such as might arise, for example, from soft x-rays or secondary electrons emitted from the walls of the ionization chamber.

The factors which prevent precise determinations of critical potentials are well known. The initial distribution of electron velocities from the heated filament cathode is the most troublesome source of uncertainty and prevents sharp breaks in the ionization curve at the points where new critical potentials make their appearance. However, computations based on the assumed validity of the Lawrence probability law and the experimental realization of a Maxwellian velocity distribution, make it evident that under such conditions, the probability function ought to be amenable to experimental test.

Apparatus

A modified form of Farnsworth electron gun[10] was chosen as a basis for the apparatus inasmuch as it had shown itself capable of producing electron beams of an unusually high degree of homogeneity. A cross sectional view of the ionization tube, with circuit diagram is shown in Fig. 1. All metal parts were of nickel. The filament used in this investigation was of the coated type noted for its low work function and was furnished through the courtesy of the Bell Telephone Laboratories. The figure indicates the manner of connecting the filament to the tungsten leads and shows that the magnetic field due to the heating current in the filament was negligible. This was substanti-

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[3] K. T. Compton and C. C. Van Voorhis, Phys. Rev. **26,** 436 (1925); **27,** 724 (1926).
[4] T. J. Jones, Phys. Rev. **29,** 822 (1927).
[5] J. C. Morris, Jr., Phys. Rev. **32,** 447 (1928).
[6] W. Bleakney, Phys. Rev. **35,** 140 (1930).
[7] E. O. Lawrence, Jour. of the Frank. Inst. **204,** 91 (1927).
[8] A. L. Hughes and C. M. Van Atta, Phys. Rev. **36,** 214 (1930).
[9] A. von Hippel, Ann. d. Physik **87,** 1035 (1928).
[10] H. E. Farnsworth, Jour. Opt. Soc. of Amer. **15,** 290 (1927).

ally an equipotential source, since, with 1.2 amperes heating current, the potential drop across the filament was less than 0.05 volts. The accelerating potential was, in effect, applied at the center of the filament by a potentiometer arrangement across the filament battery.

O is a focussing cylinder provided with a tight fitting sleeve for the purpose of facilitating renewals of the filament. The end of cylinder *B*, to which the electrons were accelerated, was extended a sufficient amount in order to cover the filament and focussing cylinder. This arrangement prevented electrons from passing around the outside of the cylinder where they might strike the glass walls of the tube and give rise to troublesome electrostatic effects. Cylinders *B*, *C* and *D* served to control the velocity of the electrons as well as to collimate the beam. In order to prevent electrons from striking the metal walls and at the same time allow for the natural widening of the beam, the

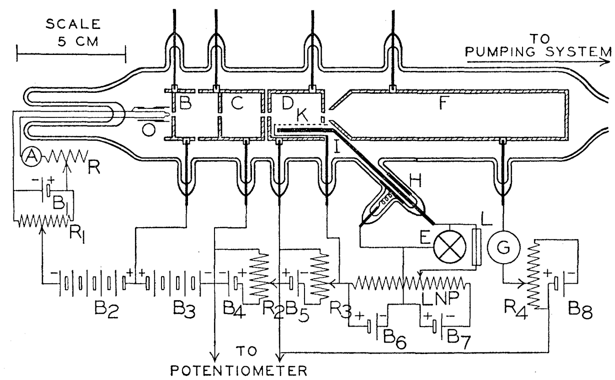

Fig. 1. Cross-sectional diagram of ionization tube showing a schematic arrangement of the electrical connections.

holes in successive cylinders were made with gradually increasing diameters. The circular opening in cylinder *B* was crossed by 10 minute nickel wires equally spaced. This made the accelerating field very uniform across the opening, and tended to prevent unfavorable modification of the velocity distribution of the emergent electrons.

It was decided to employ a Faraday cylinder to receive the electron beam inasmuch as investigations by Lawrence[11] had shown such a device to be an efficient electron absorber if its length were made sufficient to prevent reflection of slow electrons. The Faraday cylinder, *F*, was made 11 cm in length. Subsequent tests showed that it retained all entering electrons.

The usual precautions of removing occluded gases and water vapor by thoroughly outgassing the glass and metal parts, were taken.

The tube was mounted so that its axis was parallel to the lines of the earth's magnetic field. Thus there was no component of the earth's field tending to deflect the electrons from their course down the axis of the tube. In addition to this, the tube was placed at the center of a large pair of square coils. By suitably adjusting the orientation of these, and controlling the cur-

[11] E. O. Lawrence, Proc. Nat. Acad. Sci. **12**, 29 (1926).

rent through them, either the earth's field could be neutralized or they could be made to produce an axial field which would aid in defining the electron beam. Finally it was found desirable to wind a long solenoid on the outside of the tube for the same purpose.

The apparatus was kept on the pumps during all runs, the gas pressure being maintained at all times below the limits measurable on a McLeod gauge. The pressure of the mercury vapor was controlled by varying the temperature around a liquid air trap connected in the system at a point near the tube. Most of the runs were taken with a vapor pressure corresponding to a temperature of zero degrees centigrade, although some data were taken with a pressure corresponding to room temperature.

The electrometer used to measure the positive ions was of the Swann type, having a sensitivity of about 4000 mm per volt. The electron currents were detected by a Leeds and Northrup galvanometer having a sensitivity of about 2000 megohms. The potentials applied to cylinders B and C were measured by Leeds and Northrup precision voltmeters (not shown) accurate to 0.25 percent.

Experimental Method

As a rule, electrons were accelerated to B with about 15 volts velocity, retarded to C with about 5 volts velocity and given their final energy on passing into D. After colliding and producing ions in the field free space of the ionization chamber D, the electrons passed into the Faraday cylinder F, where they were collected. The positive ions formed in D, were accelerated by a small potential of a few tenths of a volt to the grid K and by a much larger potential to the ion collector I. This arrangement prevented electrons from reaching the ion collector and yet caused little distortion of the field in D. The variable accelerating potential applied to the beam as it entered the ionization chamber, was provided by battery B_4 shunted by potentiometer R_2, and its value was accurately fixed by a Leeds and Northrup potentiometer and standard cell. The method was to vary this accelerating potential in steps of 0.05 volts and to record the number of positive ions produced, as a function of this potential.

The method of measurement of the positive ion current was as follows. The collecting electrode I was attached to the free quadrant of the electrometer E and the accumulation of charge on the quadrants, was balanced by an equal and opposite current introduced by an attached india ink resistance L, of about 10^{11} ohms and a Leeds and Northrup potentiometer L. N. P. The readings of the potentiometer were then directly proportional to the positive ion current.

The velocity distribution of the electrons in the beam was determined by retarding potential measurements to the Faraday cylinder in the usual manner.

Experimental Results

Fig. 2 shows a plot of the probability law, formulated by Lawrence to explain the results of his experiments using the magnetic separation method. The equation of this probability law is:

$$P(e) = P_{e_0}\epsilon^{-10(e-e_0)/e_0} \qquad (1)$$

where e is the energy of the impacting electron and e_0 is the associated critical potential. $P(e)$ is the relative probability of production of a given type of ion for an electron of energy e, and P_{e_0} is the relative maximum probability of the several types of inelastic impacts. These relative maximum probabilities together with the associated critical potentials as given by Lawrence are:

e_0	10.40	10.60	11.29	11.70
P_{e_0}	0.25	1.0	1.4	1.15

These probabilities are based on the arbitrary assignment of a probability of 1.0 to the 10.60 critical potential.

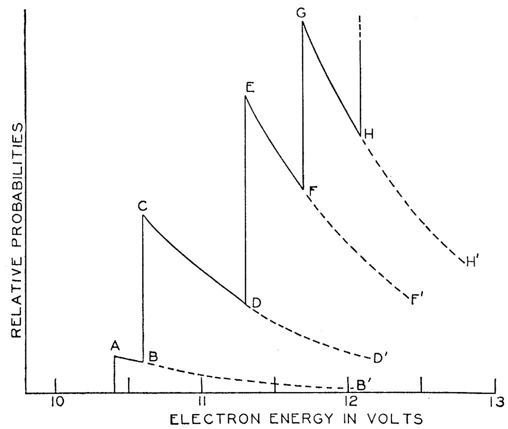

Fig. 2. Probability law of Lawrence for inelastic impacts in Hg vapor above 10.4 volts. The ordinates represent the relative probabilities of ionization of Hg vapor by electrons of energies corresponding to the abscissas. The heavy line *ABCDEF*, etc., represents the resultant ionization probability function while *ABB'* is the probability of 10.4 volt ionization and the ordinates between *CDD'* and *ABB'* represent the probability of ionization of the 10.60 volt type, etc.

It may be stated at the outset that no attempt was made to calculate the absolute value of the probability of production of an ion; that is, the number of ions formed per electron per unit path at unit pressure, divided by the total number of collisions made in this distance. Only relative values of the ionization probability were calculated in the present investigation.

$$P = I^+/I^- \qquad (2)$$

gives the relative probability of ionization where I^+ is the positive ion current and I^- is the corresponding electron current.

Fig. 3 is typical of many ionization runs taken under the best experimental conditions. The filament was operated at a dull red heat. A current of 0.92 amperes which was passed through the magnetizing coils, produced a field of about 13 gauss which helped to collimate the beam. That the beam was exceptionally narrow is indicated by the fact that the ratio of the current to the Faraday cylinder to that intercepted by the ionization chamber was 12.5/1 at the start of the run and at the end of the run no measurable current was intercepted by the ionization chamber. The black dots represent the experimental values of the relative probability of ionization (ordinate) as a function of the accelerating voltage between cylinders C and D. The liquid air trap controlling the pressure of the mercury in the apparatus, was maintained at 0° centigrade. At this temperature, the vapor pressure of mercury is 3.5×10^{-4} mm and the electronic mean free path is about 85 cm. The observed velocity distribution, which is about 0.7 volt in width, is only 0.3 volt wider than that estimated from the Maxwellian law for a filament burning at a dull red heat.

An examination of the experimental ionization curve EI indicates marked departure from the type of curves obtained by Lawrence[1] and Morris.[5] There

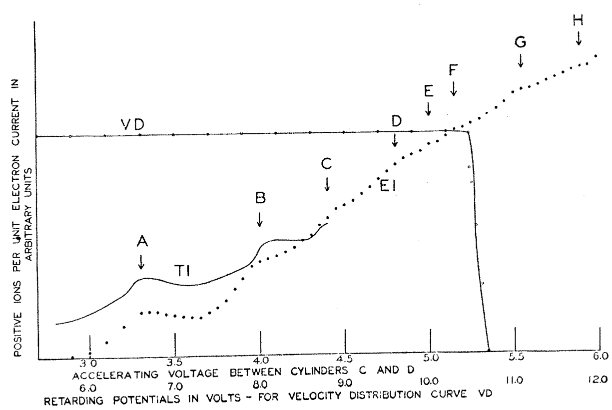

Fig. 3. The ordinates of VD are the electron currents entering the Faraday cylinder corresponding to the retarding potentials represented by the abscissas. The ordinates of EI record relative values of the ionization as a function of the accelerating potential applied to the ionization chamber, D. Curve TI is an ionization curve theoretically calculated from the velocity distribution assuming a succession of distinct types of ionization having the critical potentials 10.40, 10.60, 11.29 and 11.70 volts respectively, and the probability law plotted in Fig. 2. New critical potentials are indicated by the arrows, E, F, G and H.

is a very pronounced critical potential at the point indicated by the arrow A, another at B and less conspicuous potentials at C, D, etc. It seemed very evident from the contour of the ionization curve that a probability law of the type proposed by Lawrence, must be operative. The slope of the curve just beyond A actually passes through zero and becomes negative and again passes through zero. It was therefore decided to test the Lawrence probability law by computing the theoretical ionization curve from the measured velocity distribution, making use of Eq. (1). The results are shown by the solid curve TI. The ordinate scale for this graph has been displaced one unit in the positive direction in order to facilitate comparison with the curve EI. The agreement can be considered quite good for an experiment carried on under conditions entirely different from those of the magnetic analysis method of Lawrence, and lends strong support to his law. The fit of the two curves is especially close over the region of the first ultraionization potential (point A) as would be expected since the separation of the latter from adjacent critical potentials is relatively great and any influences due to local experimental conditions would be noticeable to a less degree. That the agreement is not better may largely be attributed to the experimentally observed fact that the velocity distribution does not remain constant as the equivalent energy of the electrons is changed. No account can be taken of such variations in computing the theoretical ionization curve. The graphical methods of differentiation and integration used in obtaining TI involve approximations which are, of course, possible sources of error in computing the theoretical curve. The curve TI is not continued over the entire region covered by EI for the reason that Lawrence assigned values of the probability coefficients P_{e_0} only for the first three of the ultra-ionization potentials. Beyond the point where TI ends, the critical potential at D and higher ones begin to contribute to the number of positive ions so that to continue the curve farther would lead to erroneous conclusions. The critical potentials beyond C are not resolved sufficiently well to enable the assignment of values of the corresponding probability coefficients with any degree of certainty. It is evident however, from considerations of their separation and the velocity distribution that the probability coefficients are of the same order of magnitude as those of A, B and C.

The proper point at which to locate a critical potential on an ionization curve has always been a moot question. Some writers argue that the proper method is to draw tangents to the curve on either side of the break point, the intersection of these two tangents giving the location of the critical potential. Others take the point of inflection where the slope goes through a maximum and some assign the critical potential to the point of inflection where the slope goes through a minimum. It seems that the proper criterion to use will depend upon the probability law which is operative in a given case together with the velocity distribution of the electrons. If one is dealing with a probability law of the kind given by Lawrence, and if one has a very narrow distribution of velocities, the second method certainly is the proper one to employ. The number of ions formed will be governed largely by the velocities of a narrow band of electrons lying near the point of inflection of the distribution curve. The slower and faster electrons on either side of this band being relatively few in number cannot contribute greatly to the ionization current. Just as the given critical potential is passed, there is a great decrease in the probability of production of the ion, which makes itself evident in the ionization curve by a decrease in slope. Thus it appears that this decrease in slope should be the most logical point to designate as the critical potential. It is on this basis that the points A, B, C, D etc., have been located. The shape of the computed theoretical curve TI indicates that this procedure is justified for the point where a new inelastic impact occurs is precisely the point where the theoretical curve shows a decrease in slope.

The values of the critical potentials observed, are: 10.60 (assumed), 11.30, 11.70, 12.10, 12.30, 12.45, 12.85 and 13.20 volts, designated by the letters A, B, C, D, E, F, G, and H respectively. That these are the correct assignments is attested both by the agreement of the computed probability curve TI, and by the fact that the separation of the critical potentials was the correct amount to agree with the values given by Lawrence. The last four mentioned critical potentials are new. Ionization of the normal mercury atom begins, of course, at 10.4 volts. This point is not indicated in Fig. 3 but would be at 3.1 on the abscissa scale of curve EI in the graph. That part of the ionization curve to the left of this point is due to the faster components of the velocity distribution in the electron beam. Since numerous runs have checked these ionization potentials, it is strongly felt that, even though the changes in slope are small in some cases, they are genuine ultra-ionization potentials. It must be pointed out also that the data are more accurate than can be shown on a graph of such small dimensions, and if the readings were plotted on a scale consistent with the precision with which the values are known, these potentials would be much more evident.

The ionization probability curve beyond 13.3 volts has been explored only casually but no evidence of additional critical potentials was noted. However, there may be many more ionization potentials in this region which are closer together and cannot be resolved with this apparatus.

Errors

There are several possible sources of error which might influence the results in this experiment and a discussion of their significance is given below.

Contact electromotive forces

These may be of two kinds, (1) contact potentials between the electron stream and various electrodes and (2) contact potentials varying over the surface of a single electrode. The first type prevents a precise calculation of any critical potential from the accelerating and retarding potentials involved. Otherwise they do no harm unless they show variations during the course of a run. Such contact potentials were always present in these experiments. Contact potentials of the type (2) are very serious if present to any appreciable degree. They prevent the collisions from taking place in a field free space, making entirely uncertain, the energy exchanges involved. The high degree of uniformity in the results secured over a long interval of time indicates that contact e.m.f's of the first type were constant and that errors due to the second type were negligible.

Diffusion of positive ions

The presence of a sheath of positive ions in the neighborhood of the filament due to the accelerating potential applied to cylinder B tended to neutralize the space charge and to favorably increase the electron emission. It is important, however, to know whether any of these were accelerated into the ionization chamber by the retarding potentials applied to the electron beam. This was tested by varying the initial accelerating potential from about 10 to 20 volts, keeping the equivalent energy of the electron beam entering D, at a value just below the ionization potential. It was found that no positive ions were collected in the ionization chamber when the initial accelerating potential was below 15 volts.

Photoelectrons

The ejection of photoelectrons from the ion collector, I, by radiation from excited atoms was reduced to insignificant proportions by making the collector of very small area. Also it was partially shielded by the surrounding grid K so that it could intercept but very little of the total radiation. That the currents measured were really positive ion currents, was demonstrated by making K slightly positive with respect to D, which caused the current intercepted by I to drop to zero.

Uniformity of field in ionization chamber

That saturation current was measured was apparent from the fact that the positive ion current remained unchanged as the potential applied between the grid K and the ionization chamber was changed from 0.05 to 1.0 volts. No reduction of the electron current to the Faraday cylinder could be detected when the small potential of 0.3 volts, ordinarily used to draw out the positive ions, was applied to the grid K.

Multiple collisions

In all cases, the mercury vapor pressure was kept so low that the electron mean free path was many times greater than the length of the ionization chamber. Even in the runs made at room temperature (25°C) the vapor pressure is 0.00184 mm and the mean free path about 9 cm. Under these conditions, therefore, multiple collisions could not have contributed to the effects observed.

Wall effects

These were rendered insignificant by designing the apparatus in such a way that the electron current intercepted by the walls of the ionization chamber was but a very small fraction of the total current intercepted by the ionization chamber. Since, in these cases, the ultraionization potentials were present with the same degree of prominence as in any data obtained, it is certain that von Hippel's suggested explanation of these phenomena on the basis of the production of secondary electrons, soft x-rays or photoelectrons, must be regarded as untenable. However, in order to further test this point, some runs were made with a magnetic field applied in such a direction and magnitude as to deflect the entire electron beam to the walls of the ionization chamber. If these ionization potentials were critical wall potentials, one should expect them to appear with unmistakable clarity under these more favorable conditions. Instead there was found but a slight suggestion of the 10.6 volts ionization potential and a faint trace of the 11.3 volt potential. This data must be regarded as giving strong support to the idea that these new potentials are genuine critical potentials of the mercury atom. The presence of the fine wire grid across the opening of the first cylinder undoubtedly gave rise to some slow secondary electrons in the beam. These, however, were included in the measured velocity distribution to the Faraday cylinder, F.

Careful attention to circuit arrangements and details of technique tended to minimize experimental errors. Individual storage battery sources of potential were used in the different parts of the circuit. Each reading of the potential between cylinders C and D was checked against a standard cell. Since the values of the positive ion current could be taken in any order desired without altering the results, it is assumed that the experimental conditions were entirely satisfactory.

The values of the critical potentials given in this work are all based on the assignment by Lawrence of the 10.60 volt critical potential which has itself, a probable error of 0.2 percent. The first three ultraionization potentials recorded above, are probably correct to 0.5 percent and the others to 0.8 percent. These values are assigned from a consideration of the details of the experimental method, reproducibility of results, etc.

Discussion of Results

As regards any attempts to explain the origin of these effects, it should be noted at the outset that the experimental method precludes any interpretation which does not regard them as genuine critical potentials of the mercury atom. Among the more likely hypotheses which have been offered were those of Lawrence[1] who suggested that they might involve ejection of one electron in the usual manner and the simultaneous removal of another electron to a higher energy state, or that they might be critical potentials of the molecule and identified with energy levels associated with band spectra. To test the first hypothesis, one must turn to the spectrum of normal and ionized mercury. The removal of one of the optical electrons from the lowest level 1^1S_0 to infinity requires, of course, 10.39 volts. To raise the other from the lowest level 1^2S to the next higher level (a metastable level $^xD_3$) in the ionized atom would require 4.38 volts.[12] Thus the minimum amount of energy required to carry through a process such as this, would be 14.77 volts. Since the electron beams in these experiments were all of energies less than this amount, this hypothesis must be rejected.

The second explanation must be regarded as equally unlikely. Both on theoretical and experimental grounds, the relative concentration of molecules to atoms, at room temperature for instance, would be very small. The heat of dissociation of the mercury molecule is but slightly larger than the mean kinetic energy of a molecule at room temperature, which would prevent any appreciable concentration of molecules. However, in order to test this point, Morris[5] tried his experiment in superheated vapor at higher temperatures. On account of the low heat of dissociation, a slight increase in temperature should greatly decrease the relative concentration of molecules to atoms, and curves taken at higher temperatures should show critical potentials of molecular origin less prominently. No such effect was observed in the case of the ultraionizing potentials.

[12] F. Paschen, Akademie der Wissenschaften Berlin, Sitzungsberichte, **2**, 541 (1928).

Von Hippel[9] has suggested that these ultraionization potentials may be due to the ionization of metastable mercury atoms. It is possible and perhaps probable that on collision with a metastable atom an electron might ionize the atom by ejecting the metastable electron and utilize any additional energy in raising the other optical electron from its lowest level to any of the possible higher levels as obtained from the mercury spark spectrum.

Assume that we have a mercury atom with one valence electron in the normal 1^1S_0 state and the other in the metastable 2^3P_2 state. The energy required to ionize the atom by removing to infinity the metastable electron, would be 4.94 volts. The energy required to raise the other electron from its lowest level 1^2S to 2^2P_1 (which is a highly probable transition) would be 6.35 volts. If we add these two numbers to ascertain the energy required to cause both transitions to occur, we obtain 11.29 volts which is precisely the value of one of the ultraionization potentials as given by Lawrence. Other possible transitions are:

	Energy required
$2^3P_2 \rightarrow \infty + 1^2S \rightarrow 2^2P_2$	12.42 volts
$2^3P_0 \rightarrow \infty + 1^2S \rightarrow 2^2P_1$	12.09 volts
$2^3P_0 \rightarrow \infty + 1^2S \rightarrow 2^2P_2$	13.22 volts.

These values correspond within experimental error to four critical potentials which have been found in this and in previous work. The close numerical agreement between the observed and calculated values lends considerable support to an explanation of the critical potentials on this basis. Of course transitions might occur to higher terms than 2^2P_2 in the spark spectrum. The difficulty in resolving these closely spaced terms, together with the decreased probabilities of transitions to such levels probably accounts for their not having been observed.

The proposed hypothesis is, admittedly weakened by the fact that the same explanation will not serve for all of the critical potentials observed. However it is not inconceivable that two different types of phenomena might be operative in giving the same kind of experimental effect. There are four observed potentials which do not fit in with a metastable atom scheme. Professor J. R. Oppenheimer has suggested, in a private conversation, that they might be due to an Auger effect in the mercury atom, that is, to processes involving excitation without ionization, spontaneous ionization occurring later, with or without a collision of the second kind.

A further test of the metastable atom hypothesis is possible from measurements of the positive ion current as a function of the electron current density in the tube. The rate of formation of metastable atoms is proportional to the density of the electron beam. Thus if the rate of disappearance of metastable atoms is constant, their concentration would be proportional to the current density. Since the number of impacts between electrons and atoms is proportional to the current density, the number of positive ions formed by impacts with metastable atoms should increase as the square of the current density. Fig. 4 shows some curves which were taken to test this point.

It is seen that the positive ion current is approximately proportional to the electron current in a range varying from 10 to 20 on the ordinate scale. This linearity cannot be said to favor the metastable atom hypothesis. At greater current densities there is a marked departure from the straight line in the direction to be expected if a secondary effect were playing a role. This deviation cannot be attributed to space charge effects, since the maximum electron current to the Faraday cylinder was only on the order of 10^{-8} amperes. Thus we can only account for this turning by assuming some secondary effect such as the metastable atom hypothesis mentioned above. If this is the true state of affairs, it is evident that the experimental conditions will greatly affect the concentration of metastable atoms and therefore the observed results. Thus the complete lack of agreement among various observers who have tested the probability law in mercury, becomes understandable.

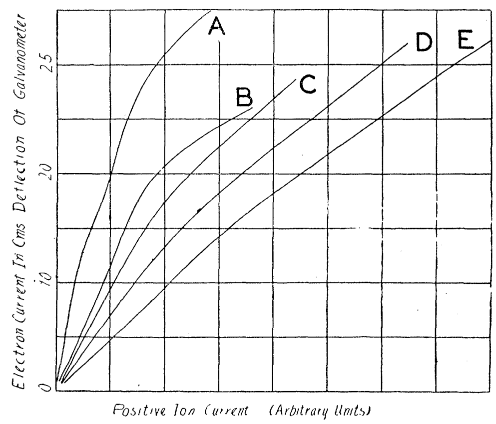

Fig. 4. The positive ion current as a function of the electron current density in the ionization chamber (ordinate scale). Curves A, B, C, D and E are taken for electron impact energies of 10.40, 10.60, 11.30, 11.70 and 12.10 volts respectively.

The double curvature exhibited by curve A near the ordinate 20, is interesting and can be explained as follows. This curve was taken for equivalent electron energies slightly above 10.4 volts. At this point the velocity distribution of the electron beam overlaps the 10.4 volt critical potential so that only part of the electron beam has sufficient energy for ionization. In the region from 0 to 17 on the ordinate scale the width of the velocity distribution remains nearly constant so that about the same fraction of the total number of electrons are producing positive ions in all cases. With increasing current density, the velocity distribution rapidly widens so that a greater relative proportion of the total number of electrons are now too slow to ionize and the rate of production of positive ions shows a decrease. At still higher current densities the curve again reverses itself showing that the velocity distribution becomes more nearly constant and secondary effects begin to predominate.

Thus the evidence secured, while not decisive, cannot be said to rule out the possibility of an explanation on the basis of metastable atoms. It must be remembered that diffusion may play an important role in determining the number of metastable atoms present in the ionization chamber at any time. If it should be true that for low current densities, a much greater number of metastable atoms are diffusing in from outside regions than are being formed in the ionization chamber itself while at higher current densities the reverse is the case, then the straight portions of the curves of Fig. 4 would be explained. The number of metastable atoms present is also dependent on their rate of disappearance as well as on their rate of formation, and one cannot be certain that this rate of disappearance is constant. The strongest argument against a metastable atom hypothesis is the fact that there would be required either a very large concentration of such atoms or that the collision cross section of a metastable atom toward an ionizing collision should be very great in order to account for the magnitude of the effects observed. Indeed, inasmuch as the metastable atoms are neutralized on striking the walls, it is difficult to see how a sufficiently large concentration of metastable atoms could exist at these low pressures in the ionization chamber. Couliette[13] showed that metastable atoms of mercury diffuse thru mercury as if the effective radius of the metastable atom is 1.5 times that of the normal atom. This is in line with the above requirement.

Professor J. R. Oppenheimer, in a private conversation, has also pointed out that on this hypothesis, one should expect ionization potentials to be found at 4.94 and 5.74 volts, corresponding to simple ionization of the mercury atom. That such potentials have never been reported, may be due to the possible inefficient production of metastable atoms at those energies.

Various types of experiments have been devised to measure the energy lost by an electron on making inelastic collisions with atoms. Foard[14] working with mercury vapor, utilized the most elaborate apparatus for this purpose. He observed but one energy loss in the region covered by these ultraionizing potentials, namely that at 11.07 volts. He attributed this to a double electron jump of some sort. His wide distribution of velocities, 1.6 volts, would have prevented him from observing energy losses corresponding to these ultraionizing potentials. In fact, the existence of a single loss at 11.07 volts is questionable. It is more likely due to the superposition of several energy losses which lie in the region covered by his velocity distribution.

Several investigators,[15,16,17,18] have recently reported the observation of a series of ultraionization potentials in mercury, covering the region of this investigation. There is, in general, good agreement in the measurements reported, and those of the present investigation. However Smith reports about twice the number of critical potentials observed by the writer while Hughes and Van Atta and Nielsen and Potter report several that have not

[13] J. S. Couliette, Phys. Rev. **32**, 636 (1928).
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been found in the present work. The reason why these several experiments differ so widely in the number of ionization potentials found, does not seem clear. Of these investigations, at least the first two showed no evidence of the Lawrence probability law but merely exhibited the ionization potentials as slight changes in slope of the ionization curve. The discrepancy in this regard, between the results of Smith and Hughes and those of the present work possibly may be due to a wider distribution of velocities in the electron beam in their experiments. Of course this possibility cannot be determined, since in their experiments, the distribution of velocities was not measured. The great difficulty the author had in obtaining a narrow distribution of velocities makes him feel that it is not very unlikely that Smith and Hughes and Van Atta did have a wider distribution of velocities than they thought. According to information received in a private communication from Nielsen, his experiment gave a qualitative evidence of a probability law of the Lawrence type. He observed a decrease in the number of positive ions with increasing electron energy at several of the critical potentials. Unfortunately the nature of his apparatus prevented a measurement of the electron velocity distribution so that he was not able to investigate the probability law operative.

The extreme difficulty in securing very narrow distributions of velocity in ionization experiments can be appreciated only by those who have worked in the field. The underlying causes of this difficulty appear not to have been generally recognized but became apparent to the writer during the course of a series of tests on the velocity distribution under varying conditions of mercury vapor pressure. When the mercury vapor was completely removed from the tube by using liquid air on the control trap, the range of velocities in the beam entering the Faraday cylinder immediately narrowed to that of the theoretical Maxwellian distribution. However, as soon as a slight amount of mercury vapor was admitted, the width of the distribution increased by about 0.2 volts. This can only be due to a series of inelastic collisions in which the electrons lose amounts of energy on the order of one or two tenths of a volt. This rather surprising conclusion has been confirmed by the writer by observation of a number of energy losses of this order of magnitude in the electron stream.

Further tests of the metastable atom hypothesis as well as detailed quantitative studies of these newly discovered low energy losses are now being made by the writer at the Physical Laboratories of Pomona College.

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