water vapor appears to be complete in the sense that the lines have been identified and the energy levels determined. The next step is, of course, to obtain with great precision the effective moments of inertia of the molecule. This will demand an adequate calculation of the rotational stretching effect, a problem which we now plan to attack. On the experimental side we are endeavoring to map the rotational spectrum of D_2O. An accurate knowledge of the effective moments of inertia of both H_2O and D_2O would do much towards making possible a precise determination of the true moments and hence of the dimensions of the molecule.

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Secondary Processes of Ionization in Mercury Vapor

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The ionization occurring in mercury vapor as the result of the impact of electrons of energy less than 10.4 volts was studied by use of a tube containing a small filament, the emission of which was limited by space-charge. The ionization produced has been studied as a function of electron velocity, bombarding current and pressure of the mercury vapor. For electron velocities above 7 volts the data are in agreement with the assumption that the larger part of the ionization is the result of ionization of metastable atoms by electron impact. Critical potentials at 8.4 and 8.6 volts are identified with the configurations $5d^96s^26p\ {}^3P_1{}^0$ and $5d^{10}6s7p\ {}^3P_1{}^0$, respectively. Another critical potential at 6.9 volts is tentatively identified as the difference between the lower metastable level, $6s6p\ {}^3P_0{}^0$, and a negative energy level, $6p^2\ {}^3P_1$. Large numbers of negative ions were found in the neighborhood of 4.9 volts. It is suggested that ionization observed in this region is due to the simultaneous formation of a positive ion and a negative ion upon the collision of a 2^3P_0 atom with a 2^3P_1 atom.

INTRODUCTION

A QUANTITATIVELY plausible explanation of the origin of the ionization which must occur in a low voltage arc was first given by K. T. Compton[1] in terms of an initial excitation of the vapor by electron impact and subsequent ionization of the excited atoms by the impact of other electrons. Various experiments in which the ionization is produced under more exactly controlled conditions than exist within an arc have since been explained on the basis outlined by Compton. Thus Franck and Einsporn[2] found critical potentials in mercury vapor corresponding to the potentials necessary to ionize the metastable levels and Smyth and Compton[3] observed a decrease in the ionization potential of iodine when it was excited by radiation from a mercury arc. Kannenstine[4] and Marshall[5] attempted to observe a lowering of the ionization potentials in He and in Hg due to the presence of metastable atoms but it was shown by Pool[6] that their results were inconclusive.

Experiments on the photoionization of mercury vapor by λ2537, discovered by Steubing[7] and later studied by Rouse and Giddings,[8] Foote,[9] and Houtermans,[10] indicate that there is probably some other secondary process in addition to that outlined by Compton which may be of major importance at least at higher pressures. It has been definitely shown that ions are produced as the result of two successive absorptions of λ2537 and that no other radiation is involved. Houtermans showed that the ions are produced probably

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[1] K. T. Compton, Phys. Rev. **15**, 476 (1920).
[2] J. Franck and E. Einsporn, Zeits. f. Physik **2**, 18 (1920).
[3] H. D. Smyth and K. T. Compton, Phys. Rev. **16**, 501 (1920).
[4] F. M. Kannenstine, Astrophys. J. **59**, 133 (1924).
[5] M. Marshall, Astrophys. J. **60**, 243 (1924).
[6] M. L. Pool, Phys. Rev. **30**, 848 (1927).
[7] W. Steubing, Physik. Zeits. **10**, 787 (1909).
[8] G. F. Rouse and G. W. Giddings, Nat. Acad. Sci. Proc. **11**, 514 (1925); **12**, 447 (1926).
[9] P. D. Foote, Phys. Rev. **29**, 609 (1927).
[10] F. G. Houtermans, Zeits. f. Physik **41**, 619 (1927).

as the result of a collision between a 2^3P_1 and a 2^3P_0 atom so that the total energy available is only 9.51 volts. This is 0.87 volt less than the energy required for ionization by a primary process. Houtermans suggested that in this case molecular ions are formed. Later Arnot and Milligan[11] found that Hg_2 ions could be produced by the impact of electrons having energies in excess of 9.5 volts.

Nielsen[12] found that negative ions were produced in mercury vapor by electron impact at 2.7, 4.9, 5.5, and 8.8 volts, probably as the result of some secondary process. Arnot and Milligan[13] also observed negative Hg ions due to the impingement of positive ions on a metal surface.

In the present paper the total ionization produced in mercury vapor by the impact of electrons having energies below 10.38 volts is studied with a view to identifying the processes responsible for the ionization.

The general experimental method consisted in studying the ionization produced in mercury vapor by bombardment with slow electrons, alone and in combination with the radiation from a low pressure mercury arc, as a function of the bombarding voltage, with various bombarding currents and pressures of vapor. Hertz's[14] method, in which the presence of positive ions increases the space charge limited current from a small filament, was used to determine the amount of ionization of the vapor.

The procedure was to obtain a curve showing the variation in the current i between the filament and the anode as a function of the accelerating voltage of the bombarding electrons, V. Ionization setting in at a given voltage would then be indicated by a change in the slope of the curve at the corresponding voltage. The curves obtained were analyzed quantitatively.

Apparatus

Figure 1 (a) shows the general type of tube employed. The tubes were made compact enough so that the complete assembly of anode, cathode and filament could be slipped down into the quartz portion of a 17 mm internal diameter quartz Pyrex graded seal which served as the envelope. This construction eliminated waxed or ground joints and made it possible to bring the mercury arc up quite close to the portion of the vapor within the tube which was to be illuminated. The oxide coated cathode was of the type described by Hertz and Kloppers.[15] The anode was of nickel, hydrogen fired and then degassed by means of an induction furnace after the tube had been pumped down and baked out. A part of one side of the anode was made of nickel gauze in order to permit the irradiation of the vapor within it. The filament was a 0.1 mm tungsten hairpin 8 mm long, generally run at a temperature estimated to be about 1700°C. Its potential was adjusted with respect to the anode so that the emission would be about 20 microamperes.

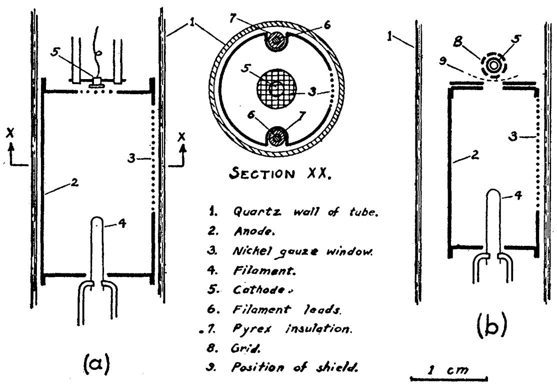

FIG. 1. Arrangement of electrodes in experimental tubes.

The tube shown in Fig. 1 (b) was designed originally to decrease any possible contamination of the anode by material evaporated from the cathode. It became apparent later that this effect was probably unimportant. However the curves obtained with this tube, due to the peculiarity of its construction, differed significantly from those obtained with the other tubes. A small shield of sheet molybdenum moved by an external magnet acting on a small iron armature shielded the anode from the cathode except when observations

[11] F. C. Arnot and J. C. Milligan, Roy. Soc. Proc. **153**, 359 (1936).
[12] W. M. Nielsen, Phys. Rev. **27**, 716 (1926); Nat. Acad. Sci. Proc. **16**, 721 (1930).
[13] F. C. Arnot and J. C. Milligan, Roy. Soc. Proc. **156**, 538 (1936).
[14] G. Hertz, Zeits. f. Physik **18**, 307 (1923).
[15] G. Hertz and R. K. Kloppers, Zeits. f. Physik **31**, 436 (1925).

were actually being made. The cathode was a nickel cylinder about 4 mm long heated by an internal coil of tungsten. The tungsten spiral grid surrounding the cathode could, for cleaning purposes, be heated electrically. The magnitude of the bombarding current was fixed by the voltage applied between the cathode and the grid which was set for a given run and was between one and four volts accelerating. The variable bombarding voltage was applied between the cathode and the anode.

There were several tubes of the type shown in Fig. 1 (a), which were practically identical except for the shape and size of their anodes. In what follows they will be referred to as "tube A." The tube shown in Fig. 1 (b) will be referred to as "tube B."

In order to increase the mercury vapor pressure above that corresponding to room temperature the tube was enclosed within an oven and connected to the pumps through a U-tube mercury cut-off one arm of which passed through the bottom of the oven. The vapor was supplied from the mercury in this arm.

A device for recording the i–V curves directly gave considerably greater accuracy than was possible by any point by point method of recording and permitted a great decrease in the time required to obtain a curve. Essentially it consisted of a galvanometer placed in the circuit between the anode and the filament and a system of lenses and mirrors so connected to the slider of the potential divider supplying the bombarding potential that a beam of light would be deflected horizontally by changes in the filament to anode current i while the vertical deflection would be proportional to the bombarding voltage V. The beam was brought to a point focus on a photographic plate. In order to make the voltage variation as uniform as possible the slider on the potential divider was driven by an electric motor through a system of reducing gears. The speed was adjusted so that a curve would be completed in about 2 minutes. The galvanometer used in the recorder had a period of 2 seconds.

Bombarding potentials were read on a large laboratory standard voltmeter reading to 15 volts full scale. It was checked against a standard cell at the beginning of the work and again toward the end.

In using the recorder an axis corresponding to zero current was always placed on the plate by short-circuiting the recorder galvanometer and running the slider of the potential divider through its travel once. Voltage marks were placed either on the curves directly or on the current axis. This was done by turning off the lamp supplying the illumination for the recorder for an instant when the hand of the voltmeter crossed each volt mark.

A mercury arc with an oxide coated cathode was used as a source of λ2537. The arc discharge of about 2 amperes passed through a tube 1 cm in diameter, having a quartz central section. A side arm held at about room temperature kept the mercury vapor pressure within the arc at a fairly low value. In use the quartz portion of the arc projected up into the oven almost against and parallel to the experimental tube.

Results

Figure 2 is a typical i–V curve taken with tube B showing the principal features of the curves

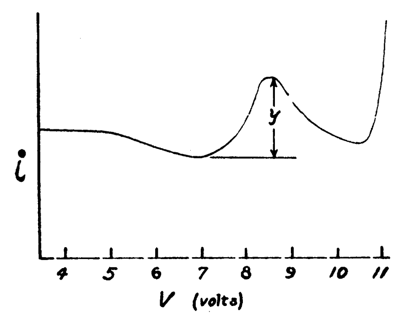

FIG. 2. Typical i–V curve made with tube B. $p=0.09$ mm. I varied between $50\mu a$ for $V=4$ volts, and $96\mu a$ for $V=10$ volts.

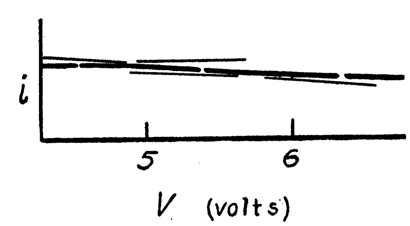

FIG. 3. Reproduction of portion of an i–V curve made with tube A showing breaks in the neighborhood of 5 volts.

studied. The voltage scale of each curve was corrected for contact potentials by translating it so that the beginning of the upward bend indicating primary ionization would occur at 10.4 volts.

Certain features of the curves may be noted:

(a) An upward rise beginning at 6.9 volts. For low vapor pressures this rise does not become noticeable until about 8 volts.

(b) A peak between 8 and 9 volts which from its shape appears to consist of two unresolved peaks at 8.3 and 8.6 volts.

(c) A decrease at 4.9 volts. This decrease was considerably larger for tube B than for tube A.

(d) A small upward break was observed on the curves taken with tube A which occurred about 0.8 volt higher than the downward break at 4.9 volts. Fig. 3 shows these breaks at 4.9 and 5.7 volts.

Figure 4 shows the effect of illumination from the quartz mercury arc on the filament-anode current. Both the curves shown here were taken under conditions which were as nearly as possible identical except that curve (a) was taken while the tube was illuminated by the arc and (b) was taken without such illumination. For purposes of comparison the upper curve has been transposed as shown by the dotted curve. The general shape indicates that the electron velocity distribution was considerably broader than in any of the curves used for locating the critical potentials. It is seen that as a result of illumination by the arc: (a) There is a general increase in the filament current. (b) The height of the peak between 7 and 10.4 volts is increased. (c) The increase in the height of this peak is relatively greater between 7 and 8 volts than at the higher voltages.

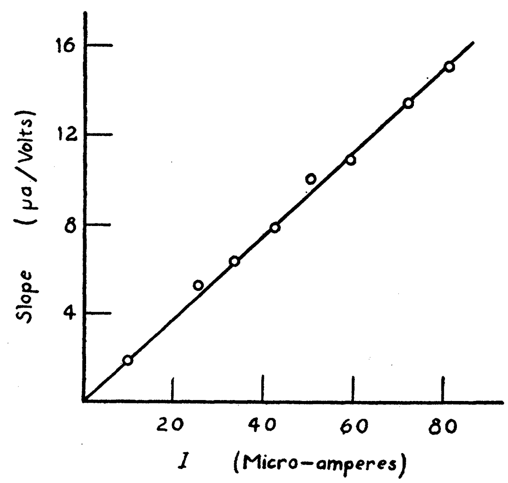

FIG. 5. Slope of i–V curves at 11.2 volts as a function of the bombarding current in tube A. $p=0.23$ mm.

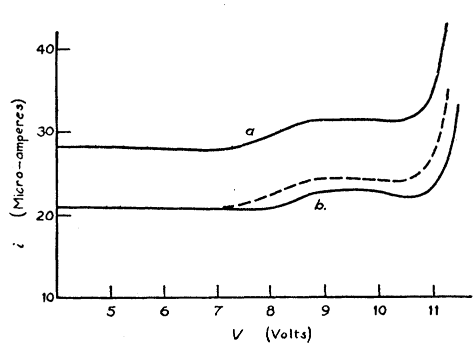

FIG. 4. Effect of radiation from the mercury arc on i–V curves. These curves were traced from data recorded automatically with tube A. (a) Arc on. (b) Arc off. For the purpose of comparison curve (a) has been transposed as shown by the dotted curve. $I=60\mu$a. $p=0.03$ mm.

As a basis upon which to test the quantitative functioning of the filament as a detector of ionization, it was assumed that almost all the ions formed by electrons whose energies exceeded 10.38 volts would be produced as the result of a primary process. The slope of the i–V curves at 11.2 volts was chosen as a measure of the change in the filament current due to the ionization. An inflection at this point reduces the effect of an error in choosing the point at which to measure the slope. In Fig. 5 this slope has been plotted against the bombarding current for constant mercury vapor pressure. The linear relation obtained is considered sufficient justification for the assumption that at constant pressure, changes in the current from the filament are directly proportional to the ionization.

In Fig. 6 the slope at 11.2 volts per unit bombarding current has been plotted as a function of the mercury vapor pressure, p, using logarithmic scales. Kingdon[16] and Foote and Mohler[17] have shown that the effectiveness of an ion in neutralizing space charge about a small filament varies inversely as the two-thirds power of the pressure. Under these conditions the effect of a given bombarding current on the filament

[16] K. H. Kingdon, Phys. Rev. **21**, 408 (1923).

[17] P. D. Foote and F. L. Mohler, Phys. Rev. **26**, 195 (1925).

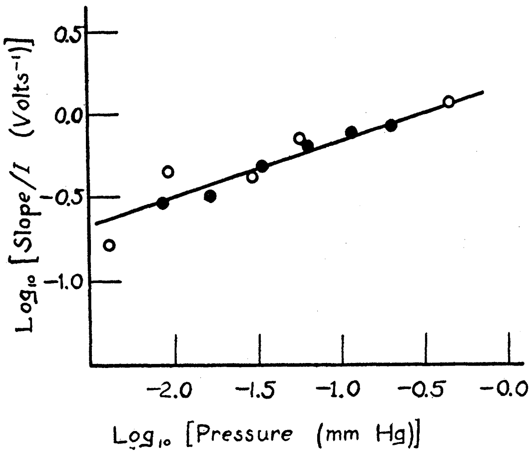

FIG. 6. Slope of $i-V$ curves per unit bombarding current as a function of the mercury vapor pressure. Points taken with two different tubes. The line through the points has a slope of one-third.

current should vary as $p/p^{\frac{2}{3}}=p^{\frac{1}{3}}$, where p is the vapor pressure. The proximity of the points of Fig. 6 to a line drawn with a slope of $\frac{1}{3}$ indicates that the points are in good agreement with this equation.

In the curve of Fig. 7 the height of the peak at 8.6 volts is shown as a function of the bombarding current I. The peak height was measured as indicated by y in Fig. 2. The curve in this illustration, however, has a minimum which is very much larger relative to the peak at 8.6 volts than any of the curves used for the data of Fig. 7 or Fig. 8. The points of these two curves would not have been appreciably changed if the peak height had been taken as the difference between filament currents at the peak and at $V=0$. The curve shown in Fig. 7 was derived from a certain hypothesis as to the origin of the peak which will be discussed later.

In Fig. 8 the peak height at 8.6 volts has been plotted as a function of the mercury pressure, the bombarding current being approximately constant.

The magnitude of the break at 4.9 volts was measured as the difference between the slopes of the $i-V$ curve at 4.5 and 5.3 volts. With tube A at a constant mercury vapor pressure and a bombarding current between 30 and 250 microamperes this break varied very nearly as the square of the bombarding current. In Fig. 9 the change of slope at 4.9 volts is shown as a function of the mercury vapor pressure for two different tubes. Because of considerable variations in the bombarding currents between the different points the changes of slope have been divided by the squares of the respective bombarding currents.

The change of slope at 5.7 volts was measured in the same manner as the break at 4.9 volts. This break was too small to permit any accurate measurements. For constant vapor pressure, it varied as some power between the square and the cube of the bombarding current for a fivefold variation in the latter.

The effect of nitrogen up to pressures of several mm was tried. The results which were somewhat erratic confirmed the conclusions obtained from mercury alone but showed nothing additional.

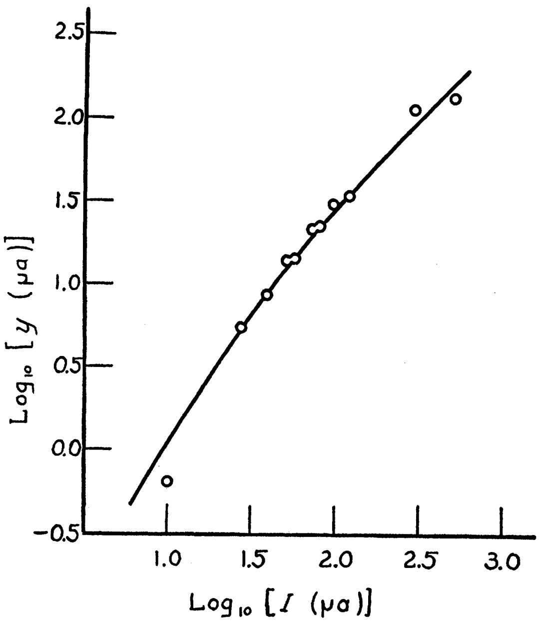

FIG. 7. Peak height at 8.6 volts as a function of the bombarding current. $p=0.23$ mm.

DISCUSSION

We may list the following as possible secondary processes by which ions might be formed:

(1) A collision of the first kind between an electron and an excited atom.

(2) A collision of two excited atoms.

(3) The absorption of a quantum by an excited atom. Unless the energy of the quantum corresponds very closely to the energy of an allowed transition from the excited state the

probability of such an absorption is very small and for the present discussion we shall assume it to be negligible.

We are here concerned chiefly with those excited levels which lie below 8 volts (Fig. 10). The lifetimes in these levels in seconds are of the order of 10^{-7} for 2^3P_1, 10^{-8} for 2^3S_1, 10^{-9} for 2^1P_1, and the lifetime of 2^1S_0 is probably within this region. These times are all considerably less than the mean free times calculated from kinetic theory which for the range of temperatures and pressures used here lie between about 5×10^{-5} and 7×10^{-7} seconds. It may be assumed therefore that the rate at which atoms disappear from these levels will be practically independent of pressure for the present range of data.

The undisturbed lifetimes of the metastable levels are very much greater, being of the order of seconds. Under laboratory conditions the lifetimes are reduced to the order of 10^{-2} to 10^{-5} seconds by the following processes: (a) Collisions of the first or second kind with other atoms. (b) Diffusion to the walls. (c) Absorption of quanta. (d) Collisions of the first or second kind with electrons.

The net effect of the first three of these

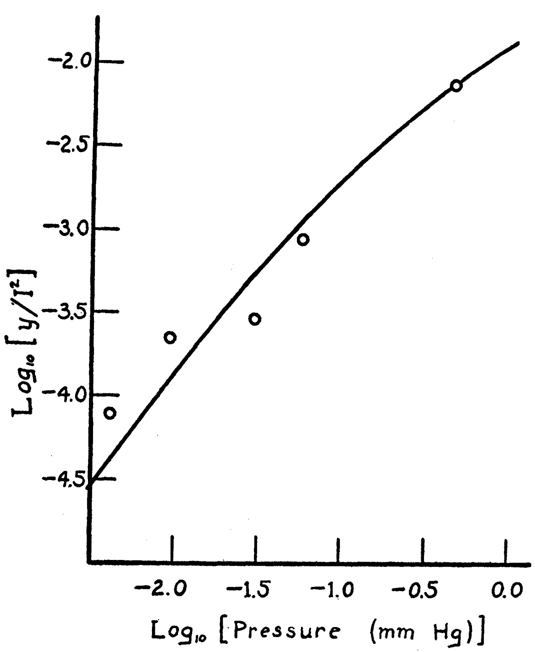

FIG. 8. Peak height at 8.6 volts as a function of the mercury vapor pressure. $I=60\mu a$ approximately.

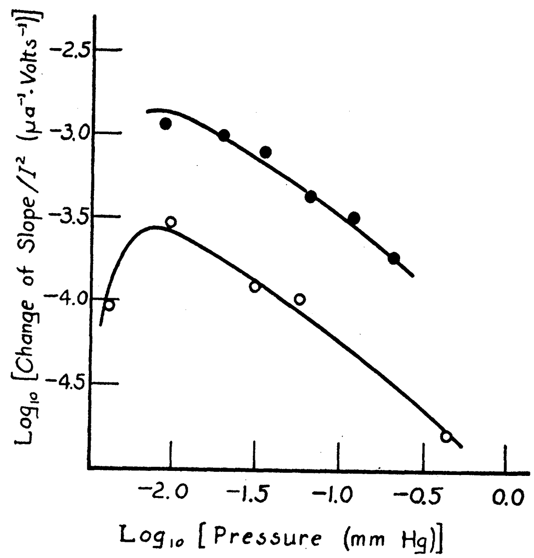

FIG. 9. Variation of the change of slope at 4.9 volts with mercury pressure.

processes may be estimated from certain experimental results obtained by Zemansky[18] who found that the decay constant, β, for the fluorescence of λ2537 in mercury vapor after the exciting radiation was removed could be expressed as:

$$\beta = aN + b/N,$$

where a is a constant, N is the atomic concentration which is approximately proportional to the pressure, and b is a constant depending on the geometry of the apparatus. On the basis of a theory advanced by Zemansky and of another developed by Samson,[19] β will also be the decay constant for 2^3P_0 atoms. In an absorption cell 1.95 cm thick used by Zemansky the two terms on the right side of the above equation were equal at a saturated mercury vapor pressure of about 0.2 mm corresponding to a temperature of the cell of 95°C. For a smaller cell, 1.3 cm thick, b was greater so that the two terms were equal at about 110°C, corresponding to a mercury pressure of about 0.5 mm. Since the internal dimensions of the tube used here were considerably smaller than the smallest absorption cell used by Zemansky, and since the pressure was always

[18] M. W. Zemansky, Phys. Rev. **34**, 213 (1929).
[19] E. W. Samson, Phys. Rev. **40**, 940 (1932).

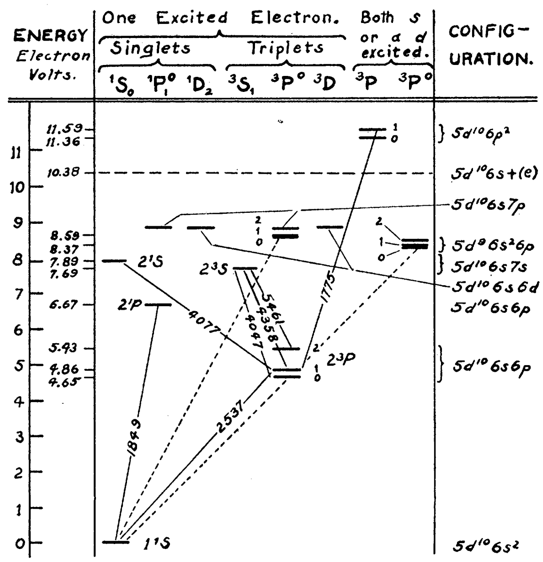

FIG. 10. Mercury energy levels referred to in this paper.

below 0.3 mm, it may be assumed, insofar as we neglect the effect of electronic collisions, that the rate of disappearance of 2^3P_0 atoms will be inversely proportional to the pressure.

The rate at which atoms are removed from the metastable levels by electronic collisions will be proportional to the bombarding current. Because of their comparatively longer lifetimes, this process may be of importance in the case of metastable atoms, while being comparatively negligible for ordinary excited states.

The general shape of the i–V curves in the neighborhood of 8 volts is very similar to the optical excitation functions of the lines λ4047, λ4358, λ5461, as determined by Siebertz.[20] These lines all originate on 2^3S_1. This suggests that the ionization occurring in the neighborhood of 8 volts is the result of an initial excitation to the 2^3S_1 level. If the energy of the bombarding electrons is increased beyond 7.69 volts where this level is first excited there will be a sudden increase in the number of atoms reaching the metastable levels because 2^3S_1 is the lowest level from which the metastable levels 2^3P_0 and 2^3P_2 may be populated by direct optical transitions. Since the difference in energy between a normal ionized atom and a metastable atom is only 5.74 volts if the latter is in the 2^3P_0 state and 4.95 volts if in the 2^3P_2 state, electrons having sufficient energy to excite the 2^3S_1 level will have more than sufficient energy to ionize atoms in either of the metastable levels. Furthermore since the lifetime of the metastable levels is such that an appreciable number of atoms in these levels may be struck by the bombarding electrons, it is reasonable to suppose that some ionization will result. The process may be treated quantitatively as follows:

Let Δi be the increase in the current from the filament to the anode as the result of this secondary process at some particular value of the bombarding voltage V.

Let n be the concentration of metastable atoms.

As before let I be the bombarding electron current.

Then since as we have already seen, the tube responds linearly to the rate of production of ions, and since the sensitivity varies inversely as the two-thirds power of the pressure,

$$\Delta i = kp^{-\frac{2}{3}}nI, \tag{1}$$

where k is a constant which depends on the tube.

If the metastable levels are supplied chiefly by radiation from the 2^3S_1 level, the rate of production will be directly proportional to the concentration of 2^3S_1 atoms. This concentration, insofar as we neglect all secondary methods of production, will be jointly proportional to the bombarding current and the concentration of normal atoms. If we neglect temperature variations, this last factor may be replaced by the pressure. Hence we have upon equating the rates of production and disappearance of metastable atoms:

$$aIp = bnI + cn/p, \tag{2}$$

where a, b, and c are constants which depend on the tube. The first term on the right side of this equation represents the rate at which electrons in the bombarding beam cause atoms to pass out of the metastable levels and the last term is the rate at which metastable atoms disappear due to other causes.[21]

[20] K. Siebertz, Zeits. f. Physik **68**, 505 (1931).

[21] Equation (2) gives the same relationship between the concentration of metastable atoms and the bombarding current as was found by Kopferman and Ladenburg, Zeits. f. Physik **48**, 15 (1928), to exist between the concentration of metastable atoms in the positive column of a neon glow discharge and the current density.

On combining Eq. (1) and Eq. (2) we have:

$$\Delta i = akI^2p^{1/3}/(bI + c/p). \qquad (3)$$

Let y be the height of the peak at 8.6 volts. Then if the ionization is due almost entirely to the process outlined, we will have:

$$y = I^2p^{1/3}/(UI + V/p), \qquad (4)$$

where U and V are constants which depend upon the tube.

Equation (4) may be written as:

$$I^2/y = (U/p^{1/3})I + V/p^{4/3}. \qquad (5)$$

Hence for constant p, I^2/y plotted as a function of I should give a straight line of slope $U/p^{1/3}$ and intercept $V/p^{4/3}$. In Fig. 11 the data corresponding to Fig. 7 have been plotted in this manner. From the slope of the line drawn through these points, $U/p = 3.0$; and from the intercept, $V/p = 57$; where $p = 0.23$ mm of mercury, and I is expressed in microamperes. These values have been substituted in Eq. (4) to compute the curve of Fig. 7.

Substituting for p its known value we obtain: $U = 1.8$ and $V = 8$. These are constants which are independent of current and pressure and depend only on the geometry of the tube and the operating conditions of the filament. The tube used for obtaining the points of Fig. 7 and the tube used for the points of Fig. 8 had filaments which were almost exactly alike, although the anodes differed in their dimensions. From the value of U and V determined by the former tube it was estimated, from a consideration of the differences in the anodes, that for the data of Fig. 8, we should have approximately, $U = 0.9$ and $V = 16$. These values were used in Eq. (4) to compute the curve shown in Fig. 8.

It appears reasonably certain that the peak cannot be due to either of the other secondary processes previously mentioned. If the peak were due to collisions of excited atoms with other excited atoms or with quanta, it would still be necessary to assume that metastable atoms were involved in order to explain the downward curvature of the points of Fig. 7, since these are the only states having lifetimes sufficiently long to make destruction by electron impact at all probable and thus result in a total ionization which varies by some power less than the square of the bombarding current. The concentration of the second constituent of such collisions, excited atoms or quanta, would vary approximately with at least the first power of the pressure because

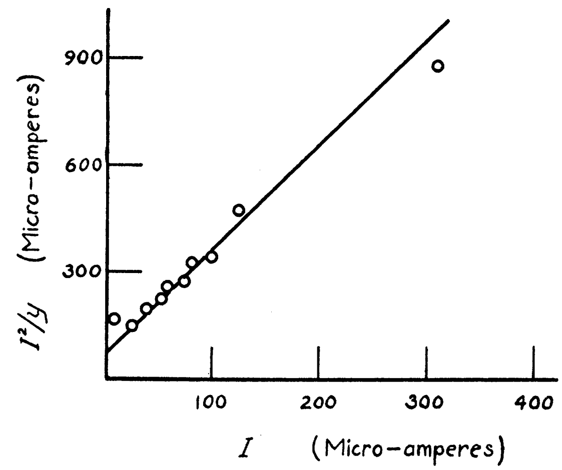

FIG. 11. I^2/y as a function of I.

the rate of production by electron impact depends upon the number of collisions which the bombarding electrons make with normal atoms. With such a mechanism Eq. (4) would be replaced at sufficiently low pressures or small bombarding currents, by an equation of the form:

$$y = (1/V)I^2p^n,$$

where $n \geqq 7/3$, and the points of Fig. 8 might be expected to approximate to a line of slope 7/3. The slope of approximately one which is actually observed agrees much better with the original hypothesis as to the origin of the peak.

It seems very probable that of the two metastable levels, 2^3P_0 must be the one chiefly involved in the processes of ionization discussed so far. The term in Eq. (2) which we attributed to destruction of metastable atoms by collisions with electrons implies a metastable state having a fairly long life. This condition is fulfilled much better by the 2^3P_0 state than by the 2^3P_2. It is principally the former level which is filled by radiation from the mercury arc so that the additional ionization produced is most reasonably ascribed to the excitation of this state rather than to 2^3P_2.

It is probable that the sharp maximum occurring in the excitation function of the level

2^3S_1 and the sharp maximum also observed here in the secondary ionization may be due to the fact that when the energy of the electrons equals or exceeds that necessary to excite the levels just above 2^3S_1, the number of atoms reaching 2^3S_1 suddenly decreases because the energy of the bombarding electrons is now taken up by the excitation to the higher levels. This hypothesis is in beautiful agreement with the shape of the peak obtained here between 8 and 9 volts. The first two levels above 2^3S_1 to which transitions from the ground state are optically allowed, and hence which might be expected to have a high probability of excitation under electron impact are $5d^96s^26p\ ^3P_1{}^0$ and $5d^{10}6s7p\ ^3P_1{}^0$ at 8.37 and 8.59 volts respectively. These voltages correspond very closely with the sharp downward breaks obtained here at 8.3 and 8.6 volts. Since these breaks occur on a portion of the curve which is rising very rapidly they give the appearance of peaks. The voltage difference between these peaks as determined from the six best $i-V$ curves obtained with tube A is 0.25 ± 0.04 volts, which is in agreement with the difference of 0.22 volt between the two $^3P_1$ terms.

If we accept as correct the foregoing interpretation of the peaks between 8 and 9 volts, their positions may be used to correct for contact potentials more accurately than is possible with the somewhat rounded break indicating ionization at 10.38 volts. On this basis the upward rise near 7 volts is found to lie at 6.90 ± 0.05 volts. This value was the average of six determinations taken from the same plates as were used to calculate the voltage differences between the peaks.

It seems reasonable to attribute the break at 6.9 volts to an ultraionization potential of the lower metastable state. The position of this break corresponds closely with the energy of 6.93 electron volts required for the transition, $6s6p\ ^3P_0{}^0 \rightarrow 6p^2\ ^3P_1$. $6p^2\ ^3P_1$ is a negative energy level having a term value of $-9789\ \text{cm}^{-1}$. This is an optically allowed transition and therefore might be expected to have a fair probability of occurrence under electron impact. Shenstone[22] has suggested that ultraionization potentials may be excitation potentials of negative energy levels which produce ions by autoionization. However, as Shenstone has pointed out, it is not to be expected that the $6p^2\ ^3P$ levels would lead to such ionization directly. Ionization would have to be preceded by a radiative transition to a lower unstable level.

The break at 5.7 volts is probably an ionization potential of the 2^3P_0 level. This agrees with the difference of 5.73 volts between the ionization potential at 10.38 volts and the excitation potential of the 2^3P_0 level.

The origin of the downward break at 4.9 volts is not entirely clear. Off-hand one might expect 4.9 volt electrons to have about the same effect on the ionization within the tube as the absorption of λ2537, which has the same energy. λ2537 excites the 2^3P_1 level and from this the 2^3P_0 level is populated by collisions with normal atoms. These are the only two levels which we would expect to be primarily excited by 4.9 volt electrons. However, it is observed that where absorption of λ2537 leads to an *increase* in the filament-anode current, the impact of 4.9 volt electrons leads to a *decrease* in the filament-anode current.

Since the magnitude of the break at 4.9 volts varies as the square of the bombarding current, it seems improbable that the effects observed can be due directly to any space charge effects of the bombarding electrons. For the same reason and also because of the reproducibility of the break with different tubes it appears very improbable that it is due to the accumulation of charges on any insulating layers which might have formed inside the anode. Electrons striking the filament and its supports might cause a slight decrease in the apparent current between the filament and anode as measured by an external galvanometer, but there would be no simple explanation as to why the effect is observed only above 4.9 volts. We are left with the conclusion that the downward break at 4.9 volts probably indicates the presence of negative ions.

Although there is not sufficient evidence to state definitely the mechanism which causes the downward break at 4.9 volts, the following hypothesis is in accord with known facts. Houtermans[10] has shown that the collision of a 2^3P_1 and a 2^3P_0 atom is probably responsible for the ionization accompanying the absorption of

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[22] A. G. Shenstone, Phys. Rev. **38**, 873 (1931).

λ2537. Suppose that the collision of these two atoms results in the transfer of an electron so that a positive and a negative ion are formed simultaneously. The minimum total energy necessary for this process would be equal to the difference between the ionization potential and the electron affinity of the normal atom. Since the total energy available in the two excited atoms is $4.65+4.86=9.51$ volts, and since the ionization potential is 10.38 volts, the reaction suggested above will be energetically possible provided the electron affinity is in excess of $10.38-9.51=0.87$ volts. Glockler[23] using an empirical extrapolation method has estimated the electron affinity to be about 1.79 volts.

We would expect on this basis that, where the excitation is produced by radiation, the filament current would be increased because the negative space charge around the filament would cause diffusion of positive ions into that region. On the other hand where excitation is produced by electron impact there will always be a large number of slow electrons which by recombination with positive ions and by their space charge effects in other parts of the tube may cause the diffusion of an excess of negative ions into the region of the filament. This hypothesis is borne out by the results obtained with tube B in which the decrease at 4.9 volts was much more pronounced than in tube A. In the former tube the bombarding electrons were shot into the anode through a fairly large opening which permitted some penetration of the field from the grid into the space where ions were being formed. This field would act to pull positive ions out of the anode and to accelerate negative ions into it thus producing a greater preponderance of negative ions in the vicinity of the filament.

[23] G. Glockler, Phys. Rev. **46**, 111 (1933).

The decrease in the magnitude of the break at 4.9 volts as the pressure is raised is probably due to a decreased effectiveness of the stray fields within the anode in separating the positive and negative ions at the higher pressures rather than to a decrease in the actual amount of the ionization.

It seems very improbable that the downward break at 4.9 volts can be due to the process discovered by Arnot and Milligan[13] in which negative ions are formed when positive ions impinge on a metal surface. The probability found for this process decreased with the speed of the positive ions and was only 1.7×10^{-5} for 10 volt ions. Thus in any tube of the type used here the number of positive ions necessary for the production of the negative ions would completely prevent the detection of the latter. Furthermore if we did accept this explanation of the downward break at 4.9 volts, it would then be necessary to explain why the negative ionization did not mask the presence of positive ions in the region above 7 volts.

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