THE FORMATION OF NEGATIVE IONS IN MERCURY VAPOR

By Walter M. Nielsen

Abstract

The method used is similar to that of Mohler. Electrons, projected along the axis of a tube between two plates were prevented from scattering by a magnetic field of 350 gauss parallel to the axis of the tube. Negative ions formed by the attachment of an electron to an atom or to a molecule were removed by suitable potentials applied to the side plates. The remainder of the current reached a circular plate at the end of the tube. With a small field between the side plates, the negative ion current was just barely observeable (1×10^{-10} amperes). With higher fields the ion current increased enormously, approaching saturation when the potential difference between the side plates was increased to between 3 and 4 volts. In this report the ion currents were of the order of 9×10^{-9} amperes. The total current was of the order of 1×10^{-7} amperes.

The ratio between the negative ion and total current decreases with increase in the driving potential for low voltages, but increases at 2.7, 4.7, 5.5, and 8.8 volts. The decrease at low potentials is similar to the results of Mohler in other gases and vapors. The cause of the break at 2.7 volts is not known. The breaks at 4.7, 5.5, and 8.8 volts are believed to be associated with the electronegative properties of the mercury atom having an electron in a metastable orbit. The total current rises rapidly with increase in the driving potential and decreases at 4.9 and 6.7 volts.

Introduction

F. L. MOHLER[1] has recently published a report on the production of negative and positive ions in a number of vapors and gases including mercury vapor. He projected a beam of electrons along the axis of a cylinder in an approximately equipotential region with a magnetic field of 100 gauss parallel to it. He then applied a positive or negative potential of one volt to the cylinder, measuring in each case the negative or positive current to it. He concluded that under the conditions of his experiment, the number of negative ions formed at low pressure was small compared to the number of positive ions formed above the ionization potential. No negative ions were observed in mercury vapor for impinging electrons having speeds less than 10.4 volts.

The present investigation is concerned with a somewhat similar attempt to study the formation of negative ions in mercury vapor. Under conditions which are believed to approximate those in the above work, similar results were obtained, but under different conditions,

[1] F. L. Mohler, Phys. Rev. **26**, 614–624 (1925).

results were obtained which are regarded as evidence for the existence of negative ions of mercury vapor.

Experimental Apparatus

The apparatus and electrical circuit are shown in Fig. 1. Electrons from a filament F were projected along the axis of a Pyrex tube by means of a potential V_F between the filament and a diaphram C. Two plates, P_1 and P_2, were placed in a skew position as shown. Electrons were prevented from reaching them by placing the tube in the core of a solenoid so that the lines of force in the region between C and a circular plate P_3 were parallel to the axis of the tube. The

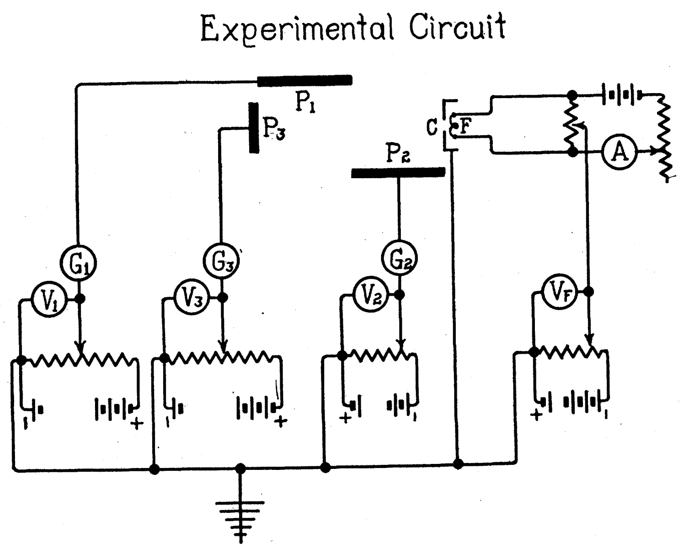

Fig. 1. Apparatus and electrical circuit.

intensity of the field was about 350 gauss. Outside the plates P_1 and P_2 and next the glass wall was a grounded gauze to eliminate extraneous surface potentials. All metal parts with the exception of the tungsten filament were of copper. The filament assembly was provided with a ground glass joint and mercury seal to facilitate replacement. The source of electrons was a tungsten spiral of one loop placed so that its elements were perpendicular to the axis of the tube.

Galvanometers and suitable sources of potential were connected to the plates P_1, P_2, and P_3. V_3 was generally a fraction of a volt higher than V_1, both being positive with respect to C. Under such conditions, electrons brought to rest as the result of inelastic collision would be attracted downward and would not therefore have a tendency to diffuse from the center of the tube as apparently occurred in the experiments of Richardson and Chaudhuri.[2] The galvanometer G_1 measured the current i_1 due to the negative charges which were able to drift to P_1 in spite of the magnetic field. This current increased rapidly with increase in the electric field between the side plates so that it was necessary to apply to them a potential difference of between 3 and 4 volts to attain saturation. The galvanometer G_2 was intended to measure the positive ion current i_2. The galvanometer G_3 measured the negative current i_3.

The vapor pressure in the tube was about .003 mm of mercury, a pressure corresponding to the temperature of the mercury seal during the observations.

Results and Discussion

With a low filament temperature, readings were taken simultaneously of i_1, i_2, and i_3, for different values of the driving potential. In most of the present work G_2 was used to indicate the ionization potential only. Dividing the current to P_1 by that reaching P_1 and P_3, a fraction R is obtained which gives the ratio between the negative ion and total current. If, as in this report, the negative ion currents are saturation currents, this number is proportional to the number of negative ions formed per unit electron current. The results are shown by the curve of Fig. 2. In this case, V_1 was 3 volts, V_3 was 3.2 volts and V_2 was zero. The potentials are corrected for initial velocity, etc., assuming the ionization potential of mercury to be 10.4 volts. The ion current was of the order of 9×10^{-9} amperes and the total current was of the order of 1×10^{-7} amperes.

The curves shown in Fig. 2, as well as those in Fig. 3 and Fig. 4 to follow, are representative of several taken over the same range under approximately the same conditions. While the currents vary somewhat because of differences in the intensity of the magnetic field, the critical points are all reproducible with the exception of a kink on the ratio curve at 7.7 volts, which did not appear on some of the curves. It did not appear on the curve of Fig. 2. It is quite astonishing that the breaks are so definite in view of the relatively large potentials on P_1 and P_3 which would be expected to blur out the effects. The fact that changes in these potentials did not produce marked changes in the critical points was proved experimentally. A change in the poten-

[2] Richardson and Chaudhuri, Phil. Mag. **45**, 337–52 (1923).

tial difference between P_1 and P_2 of 1 volt, lowered the value of V_F necessary to produce ionization by .1 volt.

That the currents observed above are in some way due to the presence of the mercury vapor was proved by removing the vapor. Carbon dioxide snow was applied to the mercury trap while the tube and connecting glassware were heated. After a few hours it was found that the negative ion current had been reduced to such an extent as not to be detectable with the galvanometer used. That such observed currents are due to electrons which have collided a number of times

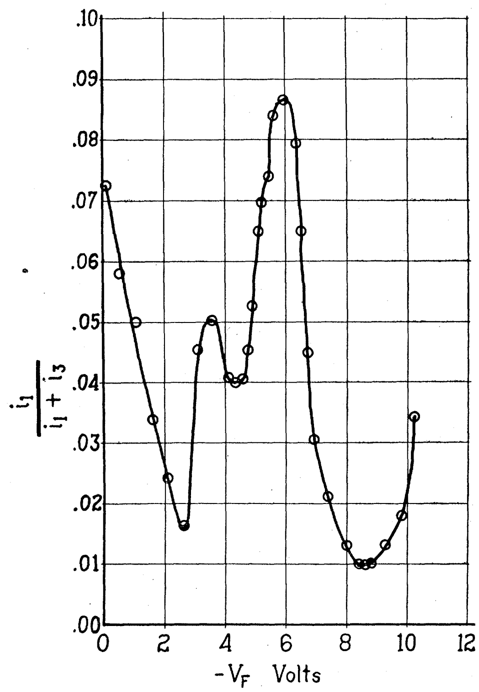

Fig. 2. Variation of the ratio of negative to total current with accelerating potential. $V_1=3.0$ volts, $V_2=0.0$ volts, and $V_3=3.2$ volts.

is quite improbable because of the low vapor pressure and because the experimental conditions, to some extent, prevented electron diffusion. One would expect that some of the electrons deflected in such a manner would have energy corresponding to V_F. To test this point, with V_1 and V_2 equal to zero, and with V_3 equal to 1.1 volts, it was found that the current to P_1 was not detectable for all values of V_F below the ionization potential. Indeed, it must be emphasized that it was necessary that V_1 be of the order of 2 or 3 volts positive in order to attract the negative charges to P_1 and cause currents of the order of 9×10^{-9} amperes as observed above. Whether or not Mohler's failure to observe these negative charges is due to this fact, is not known. In neither case do the electric fields lend themselves to computation. With a potential of 1 volt positive on P_1, the negative ion current was barely observable, being about 1×10^{-10} amperes. The radius of curvature of a 10 volt electron traveling initially at right angles to the axis of the tube in a magnetic field of the order used is about .6 mm. It seems unlikely, therefore, that the increased potential of P_1 would increase electron scattering to the walls. Because of the above facts, it seems necessary to believe that it is possible under certain circumstances for an electron to attach itself to a mercury atom or molecule.

The decrease in the ratio curve of Fig. 2 is similar to the effect observed by Mohler[1] in other gases and vapors. To explain this, he assumed that only slowly moving electrons attach themselves to molecules to form negative ions. At potentials equal to potentials of inelastic collision he observes an increase in the negative ion current in agreement with his theory. Accepting this view, one would expect an increase in the ratio curve at 4.9 volts in mercury vapor. That no kink was observed, may be due to the fact that the resolving power of the apparatus was not sufficient to distinguish it from an effect setting in at about 4.7 volts. The increase at 2.7 volts cannot be correlated with the critical potentials of the mercury atom. Possibly it is of molecular structure, although mercury vapor is generally regarded as monatomic. The mercury atom is known to have two metastable orbits corresponding to about 4.7 and 5.5 volts. The $2p_3$ orbit has a computed energy of 4.66 volts and the $2p_1$ orbit has a computed energy of 5.43 volts. Critical potentials at 4.68 and 5.47 volts have been observed by Franck and Einsporn.[3] There is evidence that an excited atom possesses an electron affinity and hence tends to form negative ions.[4] Because of these facts, the breaks in the ratio curve at 4.7 and 5.5 volts have been interpreted as being critical potentials for the formation of negative ions of mercury vapor. The rise in the curve at 8.8 volts may be interpreted to support that view. Franck and Einsporn[3] list a number of levels which they associate with an observed critical potential of 8.8 volts. The levels $3p_1$, $3d_1$, $3d_2$, $3d_3$, and $3P$ have computed potentials ranging from 8.79 to 8.82 volts. While some of these levels are

[3] Franck and Einsporn, Zeits. f. Physik **2**, 18–29 (1920).

[4] See for example Franck and Grotian, Zeits. f. Physik **4**, 89–90 (1921); Compton, K. T., Lilly, E. G., and Olmstead, Phys. Rev. **16**, 282–289 (1920); Davis, A. C., Proc. Roy. Soc. **100A**, 599–620 (1922).

metastable, those which are not, revert to levels of lower energy by the emission of mono-chromatic radiation. In particular, some of them will return to the $2p_1$ and $2p_3$ orbits, making the atom susceptible to the formation of a negative ion. An increase in the ratio of negative ion to total current would therefore be expected from this view-point when the impinging electron is able at collision to remove the valence electron to the $3p_1$, $3d_1$, $3d_2$, $3d_3$, and $3P$ levels. Since an additional electron is necessary for the formation of a negative ion, it seems quite possible that the impinging electron having lost all of its energy, would remain attached to the atom or molecule with which it collided.

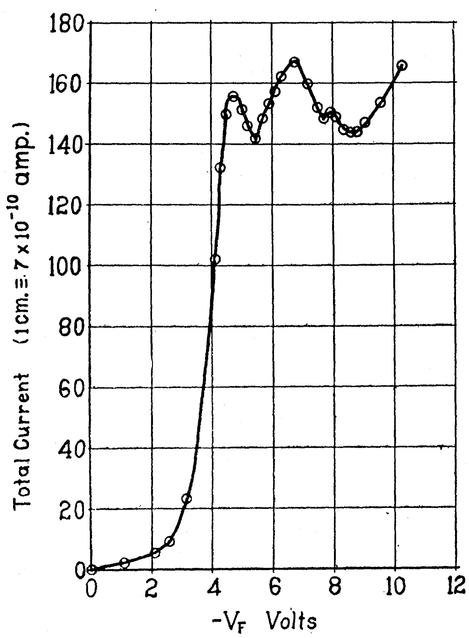

Fig. 3. Variation of total current with accelerating potential. V_1, V_2, and V_3, same as in Fig. 2.

Fig. 3 gives the variation of the total current with the driving potential. The two breaks in the curve at 4.9 and 6.7 volts correspond to the two prominent resonance potentials of the mercury atom. That the negative ions were instrumental in decreasing the total current is shown by the curves of Fig. 4, which show the variation in the total current for different positive potentials on P_3. In A, V_3 was 0 volts, in B, V_3 was 1.1 volts, and in C, V_3 was 3.2 volts. The fact that curve A shows no breaks may be attributed to the fact that possibly under such conditions very few of the electrons have energies corresponding to V_F because of space charge. With higher values of V_3, such as with *B* and *C*, the total current rises more rapidly but then seems to drop off in the region in which large numbers of slowly moving ions are formed. If now a potential is applied to P_1, such as in curve *D* of Fig. 4 and in the curve of Fig. 3, the total current is enormously increased, particularly in the region of 5 and 6 volts. In the case of curve *D*, Fig. 4, practically none of the negative ions reached P_1, although apparently some of them have been removed to a more ineffective part of the tube.

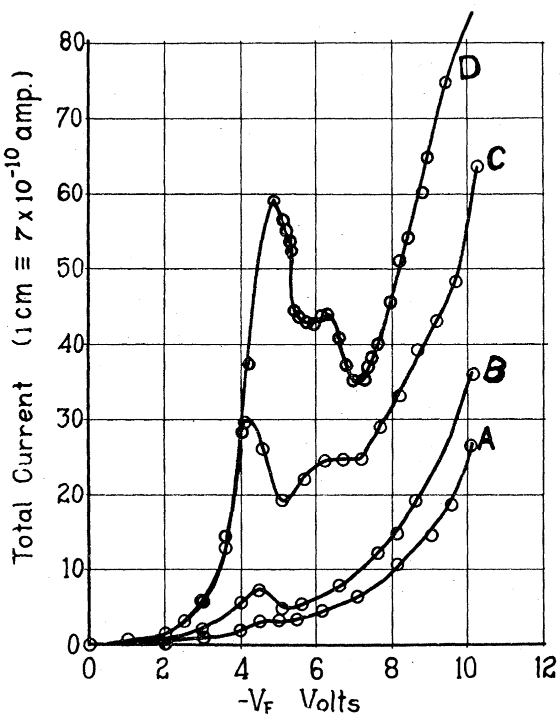

Fig. 4. Variation of total current with accelerating potential. $V_1=0.0$ volts, $V_2=0.0$ volts, in *A*, *B*, and *C*. In *A*, $V_3=0.0$ volts, in *B*, $V_3=1.1$ volts, and in *C*, $V_3=3.2$ volts. In *D*, $V_1=1.1$ volts, $V_2=0.0$ volts, and $V_3=3.2$ volts.

The drop in the curve at 5.5 volts may be associated with the increase in the ratio curve of Fig. 2 at about this potential. In the case of Fig. 3, however, the abrupt increase in the total current at this potential as well as at 8.8 volts are difficult to reconcile with the present interpretation of the data.

It is hoped that work now in progress with a tube of greater resolving power will furnish additional information on the current voltage characteristics of the electron beam and on the nature of the break at 2.7 volts.

The writer acknowledges with pleasure the encouragement and advice of Professor John T. Tate.

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February 9, 1926.