A NEW METHOD OF POSITIVE RAY ANALYSIS AND ITS APPLICATION TO THE MEASUREMENT OF IONIZATION POTENTIALS IN MERCURY VAPOR

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Abstract

A new method of positive ray analysis is described which lends itself particularly well to the study of the nature of the ions formed by single electron impact in gases, the efficiency of their production, and the measurement of their ionization potentials. The novel feature of the method is the use of the uniform magnetic field of a large solenoid so to concentrate a beam of electrons as to provide a linear source of positive ions. The ions are then pulled across the magnetic field and subjected to an e/m analysis by a suitably designed analyser.

Some preliminary results are given for mercury vapor in which the ionization potentials of Hg²⁺, Hg³⁺, and Hg⁴⁺ are found at 30, 71, and 143 volts respectively.

THE object of this paper is to describe a new method of positive ray analysis¹ which may be quite generally applied to the study of (1) the nature of the ions formed by single electron impact in gases, (2) the efficiencies of the production of these ions, and (3) the accurate measurement of their ionization potentials. Some preliminary results are given on the values of the first, second, third, and fourth ionization potentials in mercury vapor.

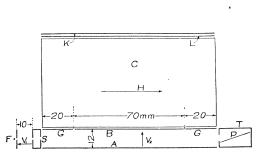
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The essential feature of the new scheme is the use of a uniform magnetic field to confine a narrow beam of electrons to a straight path of considerable length and, at the same time, to effect the separation of the ions having different values of e/m. The electrons from the filament F, Fig. 1, are accelerated by the field V_1 through the system of slits S into the region between the plates A and B where the positive ions formed are drawn out by the small field V_2 . The strong magnetic field H restricts the electrons to a very narrow beam. The pressure of the gas is such that only a small fraction of the electrons collide with molecules along the way. The beam is collected in the trap T where secondaries may be prevented from returning along the beam by applying a holding-on potential to the plate P. This beam of electrons provides a linear source of positive ions of practically uniform density. The ions are pulled out of the beam by applying between plates A and B a suitable cross field. This cross field will not, because of the magnetic field, appreciably affect either the velocity of the electrons in the beam or the position of the beam. A long narrow slit, parallel to the electron beam is cut in the plate B, and there emerges therefore behind B a wide ribbon of positive ions which may be subjected to an e/m analysis. The design of this analyzer will depend

¹ For a list of references on positive ray analysis see Phys. Rev. 33, 789 (1929).

upon the particular problem in hand. In what follows there will be described a particular form of analyser which was used to determine the first four ionization potentials of the mercury atom.

The type of analyzer chosen was one which seemed to fit best the dimensions of the tube available. It is illustrated by the diagram in Fig. 2. The magnetic field, furnished by a long solenoid, is now perpendicular to the paper. The electron beam shown by the dots is seen to be in the form of a



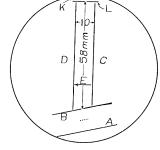


Fig. 1. Side view of apparatus.

Fig. 2. End view.

ribbon. This configuration was secured by stretching a tungsten filament wire lengthwise before the first slit (Fig. 1), this slit having dimensions 1×4 mm. The slit in plate B, Fig. 2, has the dimensions 0.25×60 mm. Hence a wide sheet of ions is shot up between the condenser plates CD. Here an electric field E is applied of a strength sufficient just to balance the force of the magnetic field on a particular type of ion. This selected ion will then travel in a straight line up through the slit in the plate E where it will be collected on the plate E. Any ion having a different value of E0 will be deflected from this path. The plates E1 and E2 are set at a slight angle to the horizontal to allow for the curvature of the ion-path before it reaches the slit in the plate E3.

In Fig. 2 let x be a horizontal axis and let y be the vertical. If a particle of charge e and mass m passes vertically through the slit in B with a velocity v_0 the equations of its path in the condenser will be

$$x = (mc/eH)(v_0 - Ec/H)[1 - \cos(eHt/mc)]$$

$$y = Ect/H + (mc/eH)(v_0 - Ec/H)\sin(eHt/mc)$$

where E and H are the electric and magnetic fields respectively and c is the velocity of light. For a particular ion to be collected on the plate K, x must vanish identically. This can only happen when $v_0 = Ec/H$. But $v_0 = (2 \, Ve/m)^{1/2}$ where V is the potential through which the ion has fallen before entering the region. Hence it follows that

$$e/m = E^2c^2/2VH^2$$
.

The apparatus was constructed entirely of copper with Pyrex glass insulation. The principal dimensions are shown in the figures. All the parts were baked out at red heat before assembling in a Pyrex tube of 9.5 cm diameter where the whole apparatus was again baked out at 400°C. One end of the tube was sealed off except for two small tubes, one leading to the pumps and the other containing the filament. The other end was closed by a

large metal plate sealed in with wax. Care was always taken to keep the wax cool. This end of the tube may be sealed off if future work demands it. It has been found possible to keep the pressure of foreign gases below 10^{-6} mm of mercury as read on the McLeod gauge while the tube was in operation.

The procedure is to fix the magnetic field and the potentials V_1 and V_2 , and then analyze the ions produced by varying the electric field E. The total ionization for a given length of path is measured by the current to the plate B and the analyzer gives the relative numbers of different kinds of ions formed.

The advantages of this method over other methods of positive ray analysis are: (1) The electron velocity is uniform and well defined, (2) the design lends itself to the study of ionization at very low pressures and very low current densities, i.e., to the study of the result of a single impact, (3) the different ions are examined by varying an electric field, all other conditions

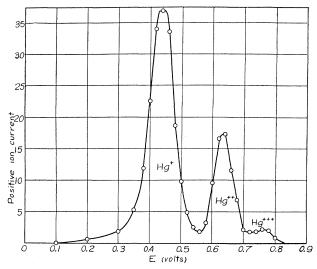


Fig. 3. A typical e/m analysis curve.

in the tube remaining constant, a feature which conduces toward great stability in operation, (4) the gas pressure throughout the tube is in equilibrium and hence may be accurately measured, (5) at the low current densities used the effect of space charge and positive ion sheaths is negligible, (6) the apparatus may be sealed up in a glass tube and thoroughly baked out. While the resolving power of the analyzer is not particularly high, yet it has proved to be excellent for the purposes for which it was designed.

IONIZATION POTENTIALS IN MERCURY VAPOR

T. J. Jones² in his work on the efficiency of ionization in mercury vapor pointed out that before a satisfactory analysis of his own results or of those of Compton and Van Voorhis or of Hughes and Klein could be made it would be necessary to determine for each electron speed the relative number

² T. J. Jones, Phys. Rev. 29, 822 (1927).

of ions having one, two, three, etc., charges. The analyzing system just described was designed to give information on this point and preliminary results have fixed the critical potentials for the formation of Hg²⁺, Hg³⁺, and Hg⁴⁺.

Figure 3 is a typical example of many curves obtained at different electron velocities and different pressures. In this particular case $V_1 = 100$ volts, $V_2 = 1.2$ volts, and H = 400 gauss. The pressure was that corresponding to saturated mercury vapor at $-8^{\circ}\mathrm{C}$. The electron current used was approximately 3×10^{-7} amperes. The current to the plate K was measured with a Dolezalek electrometer having a sensitivity of 1500 mm/volt. The curve shows a large number of singly and doubly charged ions and also a slight peak corresponding to the triply charged ion. Ions corresponding to Hg⁺, Hg²⁺, Hg³⁺, Hg⁴⁺ and Hg⁵⁺ have been found below 300 volts. It is believed that all these ions are the result of a single impact since the relative numbers have not been found to depend on the current density of the electrons. The chance that a single ion will be struck a second time before escaping from the beam is of the order of one in a million.

The ionization potentials of the first four ions have been measured by extrapolating to zero the curves, Fig. 4, representing the areas under the peaks as functions of the electron velocity. The first one was assumed to be at 10.4 volts in order to fix the voltage scale. The points lying on the zero

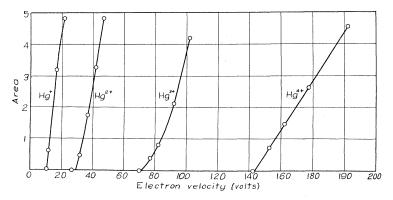


Fig. 4. Curves showing the ionization potentials of four Hg ions.

axis are not points on the curves necessarily, but merely represent runs in which no ions could be detected. The results obtained for Hg^{2+} , Hg^{3+} and Hg^{4+} are 30, 71 and 143 volts respectively. The value of Hg^{2+} is in agreement with that obtained by Smyth³ (20 volts) for a double collision.

A quantitative study of efficiencies of ionization in mercury vapor is in progress. The same type of work will then be carried out for many other gases.

It is a pleasure to acknowledge the many helpful discussions with Professor John T. Tate during the course of this work. The author is also indebted to Mr. Wm. B. Haliday for his suggestions and aid in constructing the apparatus.

³ H. D. Smyth, Proc. Roy. Soc. A102, 283 (1922).