IONIZATION BY IMPACT IN MERCURY VAPOR AND OTHER GASES.

I. THE DIRECT MEASUREMENT OF THE IONIZING POTENTIALS.

BY F. S. GOUCHER.

Introduction.—The purpose of this part of the investigation was to introduce a modification into the method for the direct measurement of the ionizing potentials of different gases, with the end in view of eliminating certain sources of error which have been present in all the applications of the method yet made.

The principle of the method we owe to Lenard;[1] it consisted essentially in the acceleration of free electrons through an electric field whose strength was varied until sufficient energy had been imparted to the electrons to produce ionization in an ionization chamber. Whereas Lenard and also Dember[2] used photo-electric electrons as the means of producing the ions, those emitted from a hot filament have been used by v. Baeyer,[3] Franck and Hertz,[4] and Pawlow.[5] In all cases, however, the exact point at which ionization set in was rendered doubtful because of a lack of homogeneity of velocity among the electrons. This lack of homogeneity arose in consequence of two causes in the cases where the hot filament was used, viz., the *IR* drop of potential along the wire, and the initial velocity of the electrons themselves due to the high temperature of the filament.

Measurements carried out by Franck and Hertz and also by Pawlow for the determination of the actual distribution of velocity among the electrons when they were accelerated through a definite applied field, revealed the fact that there was always a considerable number having a velocity of one volt or more greater than the velocity corresponding to the field applied. This amounted to 5 per cent. of the number having a velocity corresponding to the applied field, in the case of the measurements made by Franck and Hertz and considerably more in those of Pawlow.

[1] P. Lenard, Ann. d. Phys. (4), 8, 149, 1902.
[2] H. Dember, Ann. d. Phys. (4), 30, 137, 1909.
[3] O. v. Baeyer, Verh. d. D. Phys. Ges., 10, 96, 1908.
[4] Franck and Hertz, Deutsch Phys. Ges., Vol. 15, p. 34, 1913.
[5] Pawlow, Proc. Roy. Soc., Vol. 90, p. 390, 1914.

Although in both of these cases the majority of the electrons had velocities corresponding to the voltages applied and the effect of the small number having excess velocity could not have been large, yet if a knowledge of the absolute value of the ionizing potentials of the different gases measured is desired this lack of homogeneity is sufficient to render the value uncertain, as was pointed out by Franck and Hertz. The criterion for the amount of correction necessary in consequence of this is the constancy of the corrected value under different experimental conditions of temperature of the filament and pressure of the gas.

It therefore seemed desirable to minimize these two sources of error: and it was with this purpose in view that this part of the experiment was undertaken. The modification introduced was that of obtaining the electrons from an equipotential hot surface, of sufficiently large area to furnish at relatively low temperatures enough electrons for the measurement.

The method, thus modified, was to be applied to the determination of the ionizing potentials of several gases and in particular mercury vapor.

A direct determination of the value for mercury vapor seemed desirable because the values already obtained by Franck and Hertz[1] and Newman[2] have been recently called in question in a paper by J. C. McLennan,[3] on the ground that if his interpretation of the Bohr hypothesis be correct, then the interpretation put on their experiments by Franck and Hertz and Newman could not be correct.

Franck and Hertz showed that impacting electrons lost their energy at $4.9 \pm .1$ volts, whereas below that value the impacts were elastic, they therefore considered this equivalent to ionization and that 4.9 was the value of the ionizing potential in mercury vapor. It was also shown by them[4] that under these conditions—the impacting electrons having an energy corresponding at least to 4.9 volts—the single line spectrum $\lambda = 2536.7$ Å.U. was emitted. Further that the value of voltage yielded by the quantum relation $Ve = h\nu$, when ν had the frequency corresponding to this wave-length, was exactly 4.9 volts.

McLennan and Henderson[5] extended this work and showed that for the elements Hg, Cd, Zn, and Mg, a single line spectrum was produced, by the application of a certain minimum energy, and further that at a certain value of energy greater than this the many-lined spectrum set in. This latter, in the case of Hg vapor corresponded roughly to the value

[1] Franck and Hertz, Verh. d. D. Phys. Ges., 16, S. 457, 1914.

[2] Newman, Phil. Mag., Vol. 28, pp. 753–756, Nov., 1914.

[3] McLennan, Proc. Roy. Soc., *A*, Vol. 92, 305, 1916.

[4] Franck and Hertz, Verh. d. D. Phys. Ges., Vol. 11, p. 512.

[5] McLennan and Henderson, Proc. Roy. Soc., *A*, Vol. 91, 485, 1915.

calculated from the quantum relation when the value ν was taken to correspond to the limiting line, $\lambda = 1188.0$ Å.U. of the Paschen series, $\nu = 1.5$, S — m, P.; whereas the line $\lambda = 2536.7$ Å.U. corresponded to the first member of the Paschen series $\nu = 2$, ρ — m, S. It was argued by McLennan that in the light of the Bohr hypothesis ionization could not be said to have taken place until sufficient energy had been applied to cause the atom to emit its many-lined spectrum including the head of the series; in which case the value 4.9 volts could not be correct.

Although the method used by Franck and Hertz did not show directly whether negative electrons had been set free from the atom or not, the direct method does; and it therefore seemed advisable to make a careful measurement by the direct method as modified in this experiment.

Apparatus.—The essential feature of the modification introduced into the method was the equipotential surface electron source,[1] a sectional view of which is shown in Fig. 1. A platinum thimble T — 7.6 cm. long, .95 cm. in diameter and .01 cm. thick—was heated by a tungsten spiral H, suspended within it. T was sealed into the glass part G, at V; K being merely a support for other parts of apparatus.

The heater required about 30 watts' power, and heated the complete upper half of the thimble to a uniform temperature. The leads of the heater consisted of a heavy copper wire R and a thin copper sheath C insulated from R by a glass capillary tube I. One end of the tungsten spiral was attached to R and the other to a loop in the upper end of a tungsten wire support, S, which in turn was fastened to C. The wire support fitted the thimble T closely touching it at two points only, but these were corresponding points in a divided circuit so that no potential difference existed between them. Consequently T could be maintained at any desired potential by means of the lead wire W in metallic contact with it; the current used in heater being furnished by an insulated storage battery. M was a mica cylinder surrounding C, insulating it from T and serving to keep it concentric with T. Further, it is evident that the sheath C was practically at the same potential as T and prevented the field within it due to the IR drop along the spiral from having any effect on the electrons given off from T.

Fig. 2 shows the complete assemblage of parts as it was used for making the measurement in Hg vapor. The essential features are the electron source T; a fine platinum gauze G completely surrounding it; and a collecting electrode E of thin sheet aluminum supported and insulated by a quartz tube sealed into the side arm of the enclosing vessel.

[1] The suggestion of the use of a separate heater was given to me by Prof. J. H. Morecroft, of the Department of Electrical Engineering.

All joints S were of De Khotinsky cement excepting G' which was glass.

The parts were so designed that these joints were at some distance from the main body of the vessel, on account of the heat from the heater itself, and because the measuring chamber had to be heated to a temperature of 60° to 70° in order to obtain sufficient mercury vapor density.

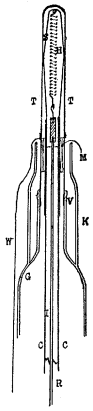

Fig. 1.

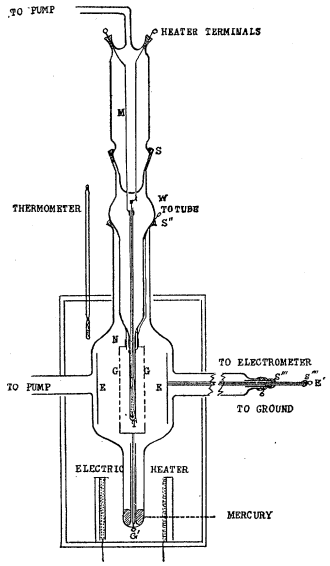

Fig. 2.

Also it is seen that the glass parts holding the thimble T and supporting the heater terminals could be separately removed, for convenience in replacing heater, lime coating cathode, and inserting liquid mercury in vessel.

The relative dimensions of the apparatus can readily be estimated from the drawing; given that the distance from T to G is about .8 cm., and that from G to E 2.5 cm. The supporting electrode EE' was about 30 cm. in length.

The double wall represents an asbestos lined box entirely enclosing the vessel and containing an electric heater and supporting a thermometer.

The two exhaust tubes of the vessel were connected through separate stopcocks to a Gaede molecular pump, and a McLeod gauge. The tube from the main vessel contained a large pentoxide drying tube and a freezing out tube.

The electrical measurements were made by a suitably shielded electrometer of the Dolezalek type, and sensitive to about 1,000 div. per volt,

used in connection with a variable air condenser and Wolff potentiometer. The potentials were applied by means of dry cells and suitable potentiometer connections, and were measured by a Siemens and Halske standard voltmeter.

I would here like to express my thanks to the Research Laboratory of the General Electric Company which so kindly furnished the tungsten used in this apparatus.

Method.—The method of measurement was essentially that employed by Franck and Hertz and Pawlow.

With suitable conditions of gas pressure within the vessel, the electrons were accelerated through the gauze, under different applied fields, until positive ions were formed in the region beyond. The fields were so arranged that the positive ions were drawn to the collecting electrode, their rate of formation being measured. This positive ion current was determined for a series of values of accelerating field and plotted in the form of a curve, the point where this current curve cut the voltage axis giving the value of voltage at which positive ionization set in under these conditions.

The determination of the distribution of velocities among the electrons for a given accelerating voltage was obtained by measuring the negative electron current as a function of an opposing field applied between the gauze and the collecting electrode, and plotting in the form of a curve. This curve was graphically differentiated and a new curve plotted, giving the relative number of electrons having velocities corresponding to the different opposing fields. The pressures used were, of course, very low and the accelerating voltage was always less than the ionizing voltages for the gas present.

Experimental Results.—The gain in homogeneity of velocity among the electrons accelerated by a given applied field, from the equipotential surface electron source, over that obtained from the hot wire is best shown by a comparison of the velocity distribution curves obtained under similar conditions.

Fig. 3 shows such a comparison. Curve (*a*) represents the velocity distribution among the electrons from the equipotential surface source when accelerated by a field of 7.5 volts, in hydrogen below .005 mm. pressure; the total electron current being taken as 100 per cent. Curve (*b*) shows the distribution obtained by Pawlow under like conditions.

It is seen that at the pressures used over 70 per cent. have velocities corresponding to the applied voltage in the case of (*a*) whereas less than 35 per cent. have the corresponding velocity in the case of (*b*); further, the number having a velocity corresponding to .5 volt greater than the

applied field in the first case was too small to be measured, whereas a measurable amount have velocities corresponding to at least 2 volts more than the applied field in the second case.

From this it can be concluded that a very high percentage of all the electrons emitted from the equipotential surface electron source have practically a zero velocity of emission; and that consequently initial

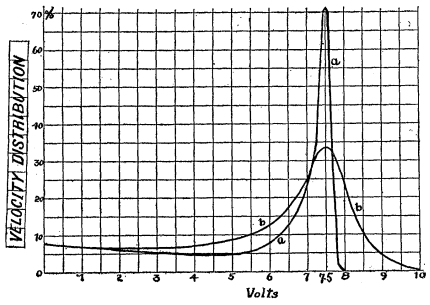

Fig. 3.

conditions approximate more closely those necessary for the determination of the absolute value of the ionizing potential than they do with a hot wire as a source.

The positive ionization curves obtained under such initial conditions of electron source show that a considerable variation of the temperature of the same will produce no change in the break point although increasing the temperature unduly will cause ionization to set in at lower voltages as would be expected. This indicates that under these conditions no correction need be made for the effect of those few electrons having initial velocities greater than zero. Similarly the curves show that changes of pressure do not affect the break point.

Fig. 4 shows two curves obtained with hydrogen present in the tube, the pressure being the same for each at .01 mm. Hg and the temperature of the electron source being varied T_2 greater than T_1. Fig. 5 shows two curves taken under the same conditions of electron source but different conditions of pressure.

The agreement and invariability of the break point at about 10.25 volts would indicate that this value corresponded closely with the absolute value of the ionizing potential for this gas, although Franck and Hertz and also Pawlow found 11 volts for hydrogen. That this was due to the pure hydrogen was considered at first to be highly probable since the hydrogen was obtained electrolytically and the constancy of pressure showed that the amount of gas given off from the hot source was extremely small. That mercury vapor had any effect was con-

sidered unlikely since no mercury had ever been in the vessel when these measurements were made and the freezing tube between the vessel and the McLeod gauge was kept immersed in an ice and $CaCl_2$ mixture. Further, it was assumed that since the ionizing potential of mercury vapor had been found to be 4.9 volts, its effect, if present in sufficient

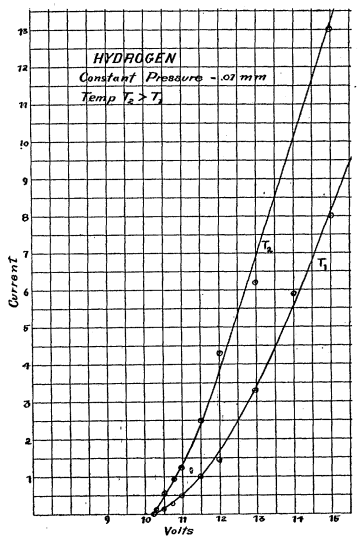

Fig. 4.

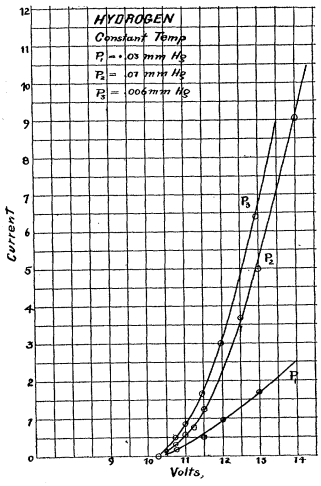

Fig. 5.

quantity, would have taken place below 10 volts. However, in the light of later results as will be pointed out, it does not seem unlikely that the slight amount of mercury vapor present, even though considerably below .0001 mm. pressure, could have been responsible for this value 10.25 ± .1 volts.

Nitrogen.—Fig. 6 shows a similar set of curves for nitrogen obtained under conditions of constant pressure, viz: 0.01 mm. Hg, but with a different temperature of the source for each curve, T_3 being greater than T_2 and T_2 being greater than T_1. Here again as in the case of hydrogen the break point is the same for the three curves within a small range; and this occurs at about 7.4 volts, which is very close to the value obtained for nitrogen by Franck and Hertz, viz: 7.5 volts. The nitrogen used was made by the department of chemistry according to their most refined methods and was considered by them to be quite pure.

Mercury Vapor.—Fig. 7 shows the set of curves obtained in the case of mercury vapor, in which curves $T_1T_2T_3$ were obtained with different temperatures of the electron source, T_3 being at the highest temperature. The velocity distribution curve shown in Fig. 8 was obtained with the

source at the temperature corresponding to that used when the curve T_2 was obtained.

For measurements obtained in mercury vapor the platinum thimble

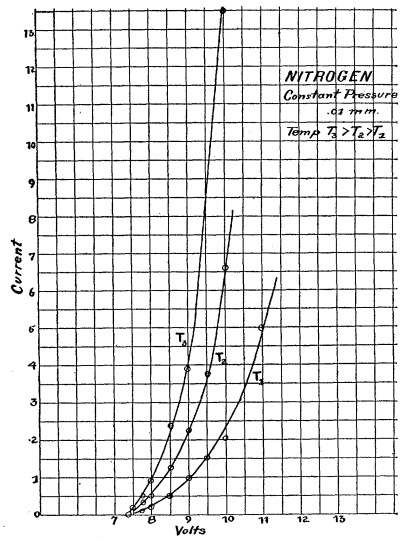

Fig. 6.

was coated with CaO and heated for a long time to free it of gases—mercury having been inserted into the tube as is shown in Fig. 2. The temperature of the whole vessel inside of the asbestos-lined box was brought up to about 55° for an hour or so before the measurements were made. Also the molecular pump was kept running to carry away traces of gas given off from the source and the walls of the vessel.

It is to be noted that the curves thus obtained are very steep, making very abrupt breaks at the voltage axis. This is what we should expect in the light of the fact that the impacts between electrons and molecules of mercury vapor have been shown to be elastic, when the electrons have an energy less than that necessary to produce ionization. For under this condition practically all the electrons given off by the source will be available to produce ionization as soon as a sufficient field has been applied, which is not the case when the impacts take place in the more non-elastic gases as hydrogen and nitrogen.

The break points in this case take place in a region between 4.8 and 4.9 volts which is in good agreement with the value 4.9 volts obtained by Franck and Hertz by their method and the value given by calculation from the quantum relation $Ve = h\nu$, where ν is the frequency of the

line spectrum emitted $\lambda = 2536.7$ Å.U., as pointed out by Franck and Hertz.

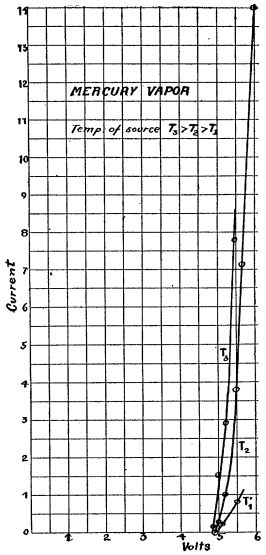

Fig. 7.

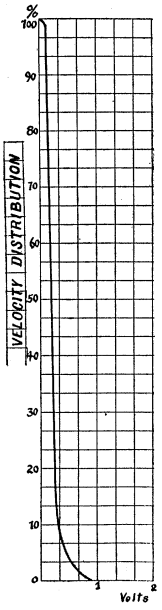

Fig. 8.

This furnishes then, additional evidence in support of this value as the true ionization potential for mercury vapor.

II. The Form of the Ionization Curve over a Range Greater than Twice the Ionizing Voltage.

Introduction.—The purpose of the second part of this investigation was to secure experimental data on the form of the current curves over a range greater than $2V_0$, where V_0 is the ionizing potential, both in the cases of elastic and non-elastic gases.

The theoretical form of the current curve for the case of a non-elastic gas has been given by Bergen Davis,[1] for a range of voltages extending from V_0 to $3V_0$.

Although the theoretical form was not worked out for the case of elastic gases, it was thought advisable to obtain data on the curve shape for an elastic gas under similar conditions to those obtaining in the case of the non-elastic gas.

Apparatus.—As the theoretical form of the curve given by Prof. Davis was expressed in terms of applied voltages, dimensions of the

[1] Bergen Davis, PHYS. REV., N. S., Vol. V., Feb., 1915.

apparatus, and pressure of the gas; it was convenient to make the dimensions of the apparatus to conform to the dimensions assumed for the calculation of a specific case as given in his paper.

To do this it was necessary to modify the form of measuring vessel to that shown in Fig. 9. The cylindrical form of electrodes could not be used, since the assumptions made in the theory were that the electrons were emitted from a plane surface with no initial velocity of their own; that they were accelerated through a gauze parallel to the electron source; and that the positive ions formed were collected by a collecting electrode also parallel to the source. The distances in the specific case calculated were taken as 1 cm. between source and gauze and 1 cm. between gauze and collecting electrode.

The vessel therefore was made to fulfill these conditions. The platinum thimble electrode T was used as before excepting that in this case only the upper end of the thimble was heated, and a guard ring P of platinum foil was supported in the plane of the end by means of a thin aluminum cylinder supported by the glass part K. (of Fig. 1). This guard ring was in electrical contact with T. The platinum gauze G and the collecting plate electrode E were each parallel to the plane of the guard ring P; G being 1 cm. distant from both T and E. In other respects the vessel was similar to that used in the first part of the experiment.

Experimental Results.

(*a*) *Case of Non-elastic Impacts.*—The gas used in this case was hydrogen, because of the possibility of maintaining its pressure very uniform throughout a series of measurements. This was done by means of a stream method; the hydrogen was allowed to pass through a palladium tube—heated by an electrical heater—at such a rate that, with the pump running continuously, the pressure did not vary over quite a considerable period of time. The pressure was chosen so that the value of the mean free path of the electron for this pressure was the same as the value postulated in the calculation of the specific case by Davis. In this way the conditions were, as nearly as possible, made to comply with all the assumptions postulated in the case calculated.

It was found, however, that the number of electrons getting through the gauze at very low pressures varied with the voltages so that the gauze absorbed electrons, consequently the curves obtained under these conditions had to be corrected to correspond to the conditions of a non-absorbing gauze. This was done by getting the percentage change of total electron current getting through the gauze for the range of voltages used and correcting the curve shape accordingly.

The pressure used to fulfill this condition was about .03 mm. Hg. The form of the corrected curve obtained is given in Fig. 10, curve (*a*), curve (*b*) being the theoretical curve. It is seen that the agreement is

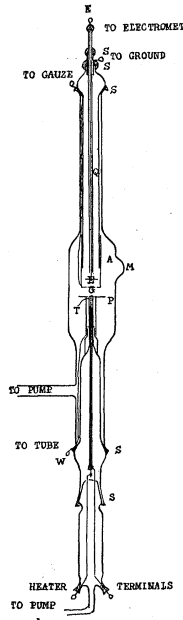

Fig. 9.

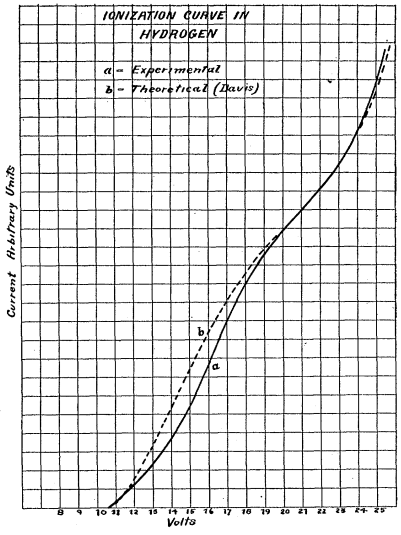

Fig. 10.

very good, and that the general form is well predicted by the theory, furnishing support for the assumptions made.

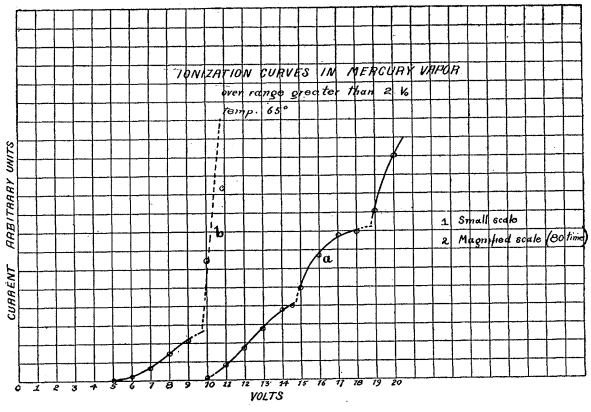

Fig. 11.

(*b*) *Elastic Impact.*—For this case the measurements were made in mercury vapor. Mercury was inserted into the tube which was sup-

ported in a horizontal position, so that the mercury formed a pool at M, and the whole was heated in an asbestos-lined box as was done in the case of the determination of the break points in mercury vapor. At first it was impossible to detect any positive ions until about 10 volts had been applied between the electron source and the gauze, when a very strong ionization set in, but it was found that by increasing the sensitivity and heating the source hotter some ionization took place between 5 and 10 volts. Thinking that the effect at 10 volts might be due to hydrogen emitted by the platinum thimble, an electrode supporting a single tungsten filament about 1 cm. in length and conducting suitable leads, was substituted for the equipotential surface electrode. This was heated for an hour or so at a very high temperature so that the residuum of gas must have been very small,—the pressure as shown by the McLeod gauge showing no variation when the filament was heated to the temperatures used in making the measurements. With this as the electron source the curves Fig. 11 were obtained, curve (b) being on a very much larger scale than curve (a). It is seen that the niches in (a) occur at approximately 3 and 4 times V_0, when V_0 is taken as slightly under 5 volts. The dotted lines signify that at these places the form of the curve is uncertain. The experimental value lying on curve (b) at the value 10 volts was about 80 times the corresponding value lying on curve (a), so that if curve (a) were plotted on the same scale as (b) it would assume a position somewhat near that shown by the dotted line.

Although from these data alone no quantitative conclusions can be drawn as to the relative magnitude of the ionization taking place at 5 and in the region of 10 volts, it however, would appear that there probably are two distinct types of ionization, as McLennan pointed out might be the case. The value at which the sharp rise occurs is in good agreement with the value 10.27 volts calculated by him from the quantum relation when the frequency was taken as the value corresponding to the head of the series spectra emitted.

It has already been shown that negative electrons are set free at 4.9 volts. Whether the marked increase in positive current be due to a greatly increased number of positive ions from which only one electron has been freed, or whether the positive charge on each ion formed has been increased due to the freeing of many electrons, it is, of course, at present impossible to say. But further experiments are in progress on this point.

It is now evident why the value $10.25 \pm .1$ volts as found for hydrogen may be due to this second type of ionization in mercury vapor, especially since this value agrees so well with the calculated value.

On account of the large quantities of mercury present in the vessel and on the electrodes as a result of the work in mercury, measurements for hydrogen, free of mercury vapor, could not be conveniently again undertaken without new apparatus. The value 11 volts obtained by Franck and Hertz and Pawlow, however, is probably correct, as they used liquid air. It is evident that in the case of the curve Fig. 9 the curve shape could be very little changed as the values 11 and 10.2 are so near together, on this scale, and further the per cent. of mercury vapor was considerably smaller in this case, due to the larger pressure of hydrogen used.

I.

Summary.—(*a*) A modification of the direct method for the determination of the ionizing potentials of different gases has been developed. As a source of electrons a platinum thimble heated from within by an auxiliary heater was employed, the electron emission thereby taking place from an equipotential surface, of comparatively large area, so that lower temperatures can be used than with heated wires. In this way the homogeneity of velocity among the electrons under a given applied field was greatly increased.

(*b*) This method when applied, gave for hydrogen $10.25 \pm .1$ volts nitrogen $7.4 \pm .1$ volts, mercury vapor $4.9 \pm .1$ volts, which with the possible exception of hydrogen are in good agreement with the values as obtained by Franck and Hertz.

II.

(*a*) By specially arranged apparatus the form of the current curve for the non-elastic gas hydrogen was obtained, extending over a range greater than $2V_0$, and found to check well the theoretical form of such curves as developed by Bergen Davis, thereby lending support to his assumptions.

(*b*) The form of the elastic gas current curve over a range equal to $4V_0$ was obtained for mercury vapor under similar conditions to those holding in the case of (*a*): the form of this indicates the probability of a second type of ionization in the region of 10 volts and that this value corresponds to that at which McLennan and Henderson have shown the many lined spectrum to be formed.

In conclusion I would like to express my gratitude to Prof. Davis, under whose supervision the experiments were carried out, and to Prof. Pupin for the facilities of the Marcellus Hartley Research Laboratory, and for his interest in the work.

COLUMBIA UNIVERSITY,
July, 1916.