THE ENERGY LOSSES ACCOMPANYING IONIZATION AND RESONANCE IN MERCURY VAPOR.

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SYNOPSIS.

Energy Losses Accompanying Radiation and Ionization in Mercury Vapor.—To make possible a *direct determination* of the distribution of electron energies after impact with vapor molecules, a special tube was constructed in which the usual grid was replaced by two diaphragms each pierced with only a single hole. These divide the tube into two chambers which can be maintained at different pressures, the one in which the collisions take place being kept at a sufficiently high pressure and the other, in which the energies of the electrons after the collisions are measured, at a very low pressure by the use of liquid air. The source of electrons was an oxide-coated platinum foil heated by radiation from a tungsten filament, and energy distribution curves were obtained for a given accelerating potential by recording the electron current as a function of the retarding potential. These curves show that below 4.9 volts the collisions are elastic but that at higher voltages energy losses of 4.9, 5.7 or 6.7 volts may occur. For example, with an accelerating field (corrected) of 9 volts, breaks occur for retarding potentials of about 2.3, 3.3 and 4.1 volts, the curve being approximately horizontal between breaks. When ionization is produced, however, the electron loses all its energy, even though this much exceeds the ionizing potential, 10.4 volts, and the electron freed by the ionization also seems to have practically no energy. The 6.7 volt type of radiating collision is not probable unless the energy of the colliding electron exceeds 8.5 volts, but it becomes far more prominent than the 4.9 volt type above 10 volts. *Comparison with spectroscopic and photoelectric data.* The observed radiating potentials correspond to the known absorption lines $\lambda\lambda$ 2536 (4.9 volts), 2330 (5.3), 2140 (5.9) and 1849 (6.7). Apparent discrepancies between these results and photoelectric data are discussed but the explanation is not yet clear.

WHEN, in 1913 and 1914, Franck and Hertz published the results of their investigation concerning the nature of electron collisions with gas molecules, there already existed a theory which accorded well with their observations, and their work and that of the many others that have worked in this field during the last decade has resulted in modifying, amplifying, but, to a surprising extent, in confirming the quantum theory as applied to atomic structure and radiation. This theory has directed much of the work in this field to the determination of the exact values of ionizing and radiating potentials, and in the case of the metallic vapors the result has almost invariably been an admirable check between these values and those predicted (by the quantum theory) from the spectral frequencies. It is surprising that comparatively little has been attempted in the way of giving precision to our conception of what actually takes place at these critical potentials. The most significant advance of this period was made when Davis and Goucher[1] showed that no ionization occurred at 4.9 volts in mercury. This changed and made much more interesting our picture of the phenomena, giving us two classes of critical potentials, the "resonating" and the ionizing potential. For the most part it has been so easy to fill in the hiatus left by experimentation with plausible extensions of the theory, that the gaps in the experimental evidence are not always apparent and yet a critical study of almost any of the investigations which have been published would show much that is not clear. Quantitative measurements are necessary before we can hope to solve all of these difficulties; yet some of the inconsistencies are so striking as to make us suspect some of the major tenets of our theory. Some of these difficulties formed the occasion for the present investigation, and as an introduction thereto it may be well to recall two recent studies of electronic collisions in mercury vapor.

In Fig. 1 is reproduced a curve, obtained by Mohler, Foote and

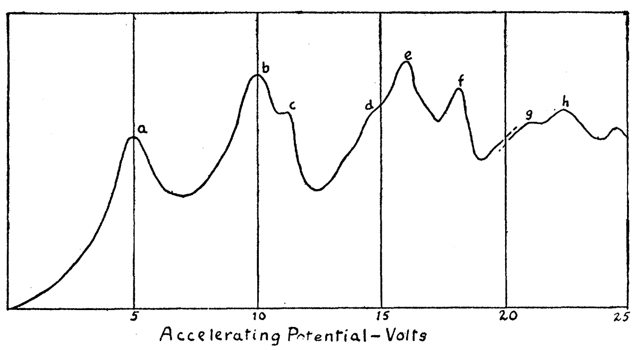

Fig. 1.

Meggers,[2] and in Fig. 2 one by Franck and Einsporn.[3] The experimental arrangements of these observers were quite similar. The electron was accelerated from the hot cathode to a first grid, then entered a constant potential region where most of the collisions were made, and was then slightly retarded from a second grid to the plate. The current to the plate is plotted as ordinate, and the accelerating potential as abscissa. The curves are in a general way similar, the differences which exist being presumably due to the extreme purity of the mercury and constancy of experimental conditions in the work of Franck and Einsporn.

Mohler, Foote and Meggers, interpreting their results, point out that

[1] Phys. Rev., 10, p. 101 (1917).
[2] Journal Opt. Soc., 4, p. 369 (1920).
[3] Zeit. der Phys., 2, p. 18 (1920).

all peaks which occur are to be explained as due to combinations of collisions of the 4.9 volt and 6.7 volt type. The inflections at *a*, *b*, and *d* are due to successive collisions of the first type; *c*, *f*, and *i* to one of the

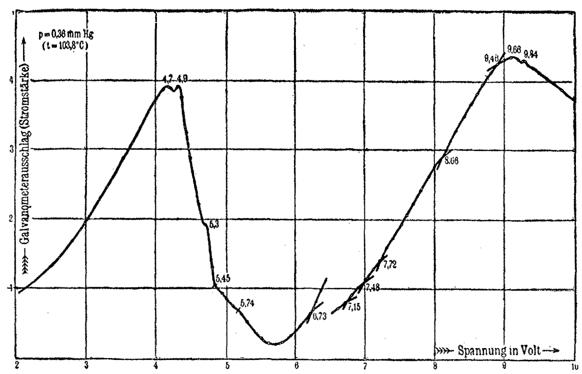

Fig. 2.

first type combined with one or more of the second; *e* and *h* to two of the first and one or two of the second; and *g* is due to three of the first and one of the second. The new type of collision (involving an energy loss of 6.7 volts) corresponds to the λ 1849 line of mercury. This line is a prominent absorption line, and while it has never been observed spectroscopically below the ionization point, photoelectric evidence that it did indeed appear at 6.7 volts had been adduced by Goucher.

Figure 1 gives strong evidence for the existence of the second type of collision with the 6.7 volt energy loss. The peaks of the curve occur at voltages which check quite closely with those obtainable from combinations of multiples of 4.9 and 6.7 volts, and all such combinations are represented *excepting 6.7 volts itself and its multiples*.[1]

Curves similar to the above, showing two resonance potentials, were obtained for other metals of the second group of the periodic table: cadmium, zinc, magnesium, and calcium; but again, except in the case of calcium, no peak was found corresponding to a single collision of the second type. To account for this it was supposed that the inflection which should have occurred here was hidden by the overlapping effect of the first resonance point. This seems an unlikely explanation since later peaks, though equally close, are readily distinguishable. Moreover, as has been noted, just as there is no peak corresponding to a single 6.7-volt collision in Fig. 1, so there is none corresponding to any simple multiple of this. And yet this type of collision when it appears in com-

[1] The agreement is not perfect. The interval between *b* and *c* and between *e* and *f* should be the same, *i.e.*, 1.8 volts, but the peak at *c* seems always to appear too soon.

bination with those of the 4.9-volt type gives very prominent peaks—peaks which are in fact more prominent than those corresponding to simple multiples of 4.9 volts, which beyond the second are quite weak.[1]

There can be, however, little question of the essential rightness of the interpretation of the peaks which occur in Fig. 1, but an explanation is needed which will account for the absence of the others and for the relative magnitudes of those which do occur. The following hypothesis, at the time it occurred to the writer, seemed to be somewhat doubtful, and yet to be the only one which would bring consistency to the above seemingly inconsistent facts: At potentials slightly above 6.7 volts, collisions of the 6.7-volt type may be possible, but are very improbable as compared with those of the 4.9-volt type. As the potential is raised, these collisions become more and more probable, and at high voltages are more likely to occur than those of the 4.9-volt type. Single 6.7-volt collisions will take place on this hypothesis if an electron has a large enough kinetic energy—say 9 or 10 volts, but these will not involve a *total* energy loss and the electron will still reach the anode; at potentials just above 6.7 volts practically no collisions of this type will occur. The usual experiment indicates only the points at which inelastic collisions involving total or almost total energy losses begin to take place, and will, therefore, give no indication of a single 6.7-volt collision. Similarly, simple multiples of this type of collision, though often occurring, will not be indicated, because, to be indicated on the curve, the last collision must be by an electron with kinetic energy of just 6.7 volts, and such an electron will lose 4.9 rather than 6.7 volts of energy. The same hypothesis makes the first collision of an electron with high velocity more probably one involving a loss of 6.7 than of 4.9 volts. This would mean that peaks corresponding to pure multiples of 4.9 volts should be relatively weak at high voltages, and Fig. 1 shows that above 9.8 volts this is indeed the case.

There are other difficulties which occur in analyzing such a curve, but they will not be dwelt upon. The interpretation of the rise in current just before *c*, followed by the extremely sudden drop at *c*, is not clear to the writer. The rise is probably due to ionization, and our ignorance of what happens at ionization is fairly complete.

Turning to the curve of Franck and Einsporn, it is seen that in a general way it corresponds to the curve dicsussed above, but shows other weaker inflection points which are attributed to other types of inelastic collisions. In the earlier part of this very interesting paper, these writers show that

[1] I have obtained curves quite similar to Fig. 1, but because of the difficulties mentioned, I was not able to convince myself at the time that they were indeed due to 6.7 volt collisions.

a photoelectric effect occurs not only at 4.9 and 6.7 volts, but at many other potentials corresponding, through the quantum relations, to prominent lines in the mercury spectrum, a result in startling agreement with the Bohr conception of radiation. The curve showing the photoelectric current as a function of the accelerating voltage is not reproduced here.

The Bohr theory leads us to expect inelastic collisions at the "radiating" potentials indicated on the photoelectric curve, and Fig. 2 shows the inelastic collisions which were found to occur. As interpreted by Franck and Einsporn, this curve does show inelastic collisions at most of the radiating potentials. It is surprising however that no agreement was found between the magnitudes of the breaks in the two curves. In Fig. 2 we find the break at 4.9 volts of predominating importance, and this has no parallel in the photoelectric curves which indicated an emission of radiation at 4.9 volts of quite the same order of intensity as formed at 4.7, 5.3, 6.7, etc. The breaks indicated in Fig. 2 are certainly in most cases very weak, and correspond at times to inflections upwards and again to downward inflections in a manner which seems quite unaccountable. Inelastic collisions should always lead to downward inflections, according to the usual interpretation of such curves. The peak at 4.7 volts is more definite. The rise by which it is followed (just before 4.9) is unexpected, but can be explained if we assume that the 4.7 collisions cease when the potential slightly exceeds the critical value. Here, as elsewhere in the interpretation of the curves, we must suppose that Franck and Einsporn had a very small velocity distribution.

When the apparatus is suitably arranged (with high vapor pressure and no constant potential region), many repetitions of the 4.9-volt type of collision can readily be obtained which show little decrease in sharpness as the number increases. It is not difficult to understand the absence of the 6.7 type of collision from such a curve, since the electron probably never gets a velocity enough in excess of 4.9 volts to excite this radiation, but it would be thought that the critical voltages which lie nearer to 4.9 would be indicated by a rapid flattening of the peaks as the number increased.

Such are some of the questions which are left unanswered by recent experimentation in this field. The answer to many of them seemed to be obtainable by a method somewhat different from that hitherto employed.

As remarked above, the method developed by Franck and Hertz and quite generally used with modifications since then, measuring, as it does, the current to a retarding plate as a function of the accelerating voltage, is only competent to show the potentials at which *total* losses of energy *begin* to take place (complicated, above the ionization point, by the ionization current).[1] It seemed desirable to alter this method by keeping the accelerating potential constant and varying the retarding potential. For any given accelerating potential, it should be possible by such a method to measure the actual distribution of velocity which exists among the bombarding electrons after a considerable number of collisions with mercury vapor.

This method is a quite obvious deviation from the usual procedure, and was used by Franck and Hertz in their early work to show that the 4.9-volt maximum was due to an energy loss of the electron. Sponer,[2] in a paper which appeared after the present work was begun, has used a similar method and has made it yield very interesting results as to the probability of inelasticity at 4.7 and 4.9 volts. However, the tube used by these experimenters was of the usual filament-grid-plate design, and with such a tube the method is very greatly limited in its applicability. It is incapable of giving even approximate velocity distribution curves, and has so little resolution as to be probably quite useless in dealing with any velocity of more than a few volts.

For the purpose which the writer had in view, it was necessary to obtain the actual velocity distribution existing among the electrons in the mercury vapor. Therefore, an attempt was made to eliminate, so far as possible, the following obvious defects inherent in the grid type of tube, when used for such a purpose:

1. The electrons enter the retarding region with only one component of their velocities in the direction of the retarding field.
2. Collisions are made in this region, so that the electrons reach the plate only by diffusion. In the work of Sponer the free path was about half a millimeter.
3. Many electrons, though reaching the receiving plate, are reflected.
4. Electrons are reflected with loss of velocity from the grid.

The apparatus as finally developed is shown in Fig. 3. An earlier form of tube was used in taking some of the observations presented in this paper. It was the same in principle, but differed somewhat in design from the final form shown. These differences will be mentioned after describing the tube represented in Fig. 3.

The glass containing tube is shown shaded. *a* represents the cathode, an oxide-coated sheet of thin platinum supported on a small quartz tube and heated from above by a tungsten spiral. This furnishes a

[1] The recurrence of peaks gives, to be sure, evidence concerning the continuity of these collisions at higher velocities but these peaks are usually too complicated to be fully interpretable.

[2] Zeit. d. Phys., 7, p. 185 (1921).

source of constant potential and one which is quite steady. *b* represents a nickel grid and wire cylinder; *c* shows a platinum cap, tightly fitting the inner tube and perforated by a small hole (0.6 mm. in diameter).

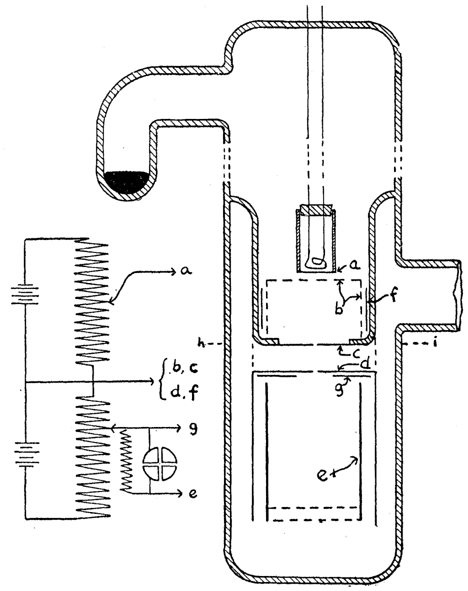

Fig. 3.

A nickel cylinder covered by a platinum disc with a similar perforation is shown at *d*, and *e* shows another nickel cylinder with its lower end covered by two layers of fine meshed nickel gauze and well insulated from other parts of the apparatus. To reduce electronic reflection, the inner walls of this cylinder are also lined with gauze. The distance between *c* and *d* is about 8 mm.

The tube is thus divided into two parts, communicating through the small hole *c*. During an experiment the upper part of the tube is electrically heated to any desired temperature (the mercury in the offset tube being somewhat underheated), and the lower part, below *h–i*, is immersed in liquid air. Under these circumstances, it is possible to maintain a high mercury pressure in the upper region, with a very much lower pressure in the region between *c* and *d*, and a good vacuum within the cylinder *e*. To avoid condensation of mercury on the nickel cylinders, the cylinder *d* was wrapped with nickel wire (not shown), and could be electrically heated while the tube was immersed in liquid air. A cylinder of thin aluminum sheet (not shown) was placed outside the nickel wire to reduce the radiation from the heated wire to the walls of the tube. A platinum cylinder is represented by *f*, placed behind the wire cylinder *b* and insulated from the hot, semi-conducting walls. This was used to take ionization curves in the usual fashion to check the behavior of the tube. *g* represents a nickel guard ring intended to be used to cut down the reflection of electrons from *e*, which electrons would have otherwise been attracted away from *e* by the field between *e* and *d*. The reflection was in fact small with this tube, and the ring had little effect.

All lettered parts had separate leads to the outside of the tube, but normally *b*, *c*, *d*, and *f* were maintained at the same potential. The electrical connections in such a case are shown in the figure. From *a* to *b* an accelerating field of any desired value is applied. The electrons enter the region below *b* with the velocity corresponding to this difference in potential, and collide with many mercury molecules here; some reach *c* and after a last collision pass through the small hole, and of these some enter the hole in *d*. A variable retarding difference of potential is established between *d* and *e*, and the current to *e* is measured as a function of this potential difference.

The earlier form of tube differed in design from that shown in Fig. 3 in that parts lettered *f* and *g* were missing, and a less direct method of eliminating the mercury vapor from the evacuated region was employed. In this case, instead of freezing the vapor out on the sides of the main tube, short side tubes were used, ending in mercury vapor traps. This tube probably gave a somewhat higher vapor pressure in *e* than did the later form shown.

An extremely small portion of the total current passes the two holes, and it is necessary to measure this current with an electrometer. A constant deflection method was used, using a shunting resistance of some 10,000 megohms of graphite on glass. This was kept dry over phosphorous pentoxide, and was very satisfactory, giving no evidence of polarization.[1]

The electrometer deflections were recorded in most cases photographically. This gave a continuous and rapid record of the current as the retarding potential was gradually increased. A Compton electrometer was used, with a period short enough to enable it to follow the impressed variations quite accurately.

The electrons passing through the perforations will reach the cylinder *e* and be measured as current so long as their velocity is greater than the

[1] In this method there is a slight correction to be made to the apparent potential of *e*, due to the *IR* drop in the shunting resistance, but this was only about 0.2 volt for a maximum deflection, and this correction has not been applied to the curves. Its effect will be appreciable only in estimating the distribution of velocities of emission which is in fact 0.1 or 0.2 volt less than that apparent from the curve.

retarding potential. The ordinate at any point on the current-retarding potential curve represents the number of electrons which had a kinetic energy greater than the retarding potential, or from the slope of the curve the number having any particular velocity is given. It is assumed that the electrons going through the holes are representative of those in the region *b*. If, then, it were possible to produce in this region electrons with kinetic energies of exactly 9 volts, the curve should be quite horizontal from 0 to 9 volts, and suddenly drop to zero. Or if half of these 9-volt electrons made collisions involving an energy loss of 4.9 volts, the curve would have a constant ordinate for retarding potentials from 0 to 4.1 volts, and then suddenly drop to a half value, which it would maintain until 9 volts. This illustrates the strong possibilities of the arrangement in resolving neighboring critical velocities, the resolution being only limited by the range of velocity distribution attainable.

In Fig. 7 the upper curve is a typical velocity distribution curve in vacuum (mercury free), taken with the tube illustrated in Fig. 3. The accelerating potential in this case was 12 volts. This curve shows a very satisfactory performance of the tube and a velocity distribution from the oxide-coated source which is mostly within a volt. The curve remains horizontal to 8 volts, then after a slight increase falls rapidly to zero, the slow electrons being lost in appreciable numbers at about 10 volts (which indicates a contact potential difference between *a* and *e* of 2 volts) and the fastest ones are lost when the potential is raised to 11 volts. The slight maximum at 9.5 volts is probably due to reflection of electrons from *e*. This reflection is less at low velocities, and consequently the number of electrons received and held by *e* is actually greater for high retarding potentials than for lower. There is every reason to believe that the drop in the curve does give very nearly the actual distribution of initial velocities.

Conditions for the Occurrence of 4.9-Volt and 6.7-Volt Collisions.

Figure 4 represents curves taken with the earlier form of tube. The mercury temperature was 140° C. in the cases of the upper two curves, and for the others 120° C., but the actual vapor pressures in *b* with this tube were somewhat less than the saturation pressures at these temperatures.[1] For each curve the accelerating potential (between *a* and *b*) is a constant, and its value corrected for contact difference between *a* and *b* is given for each curve; the uncorrected value is given in parenthesis.[2]

[1] Owing to condensation on colder walls, which was not entirely avoided in this tube.

[2] The correction for contact difference between *a* and *b* was made by taking the usual resonance curves, measuring the current to *c*. The first peak occurred at 6 volts, instead

The curves were photographed with the current to *e* (ordinate) as a function of the retarding potential between *b* and *e*; in Fig. 4 the different curves have been so placed that the corresponding drops on different curves fall approximately above one another. The abscissa marked 0

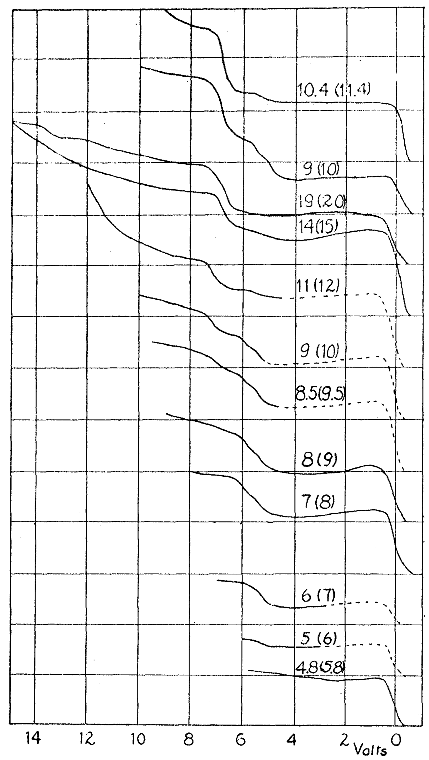

Fig. 4.

represents then for each case the potential of the source, and the other abscissas give the potential of *e* relative to the source.

However, the meaning of the curves is most easily seen, if the scale of abscissas is for the present ignored and it is remembered that the left-hand end of any curve gives the current to *e* for no retarding potential between *b* and *e*.[1] From here, as we pass to the right, the retarding potential gradually increases, the vertical rulings giving this potential in two-volt intervals. For instance, the curve labeled 6 (7) is for electrons with a corrected velocity as they enter the region between *b* and *c* of 6 volts. As we proceed from left to right on this curve, we find the

of 4.9, and ionization at 11.3 instead of 10.4, indicating a correction of one volt to be applied to the observed accelerating potentials.

[1] That is, no apparent potential difference—there is a contact difference of potential.

current at first decreases slightly until the retarding potential is 1.3 volts, when it drops more rapidly to about half its former value. As the retarding potential is further increased, the current stays nearly constant (increasing slightly) until a retarding potential of 6.5 volts is reached, when it drops rapidly to zero. (The fact that it requires 6.5 volts to stop 6-volt electrons is due to a contact difference in potential between *b* and *e*.) Of the total number of electrons passing through the hole in *d*, we see that we continue to get about half, with retarding potentials as large as 6.5 volts; the other half were lost with a retarding potential some 4.9 volts less than this—this group then had given up 4.9 volts of their initial energy by collision. The energy losses which the electrons have suffered are to be determined then by counting back from the steepest part of the terminal drop at the right end of the curve to similar points on preceding drops. Since the terminal drops come at approximately zero on the scale of abscissas, these energy losses can be read directly from that scale.

The lowest curve was taken with an accelerating potential of 5.8 (corrected 4.8) volts, which had been observed to be just less than the potential at which inelastic collisions set in. It is seen that in general the curve remains horizontal until the retarding potential is enough to overcome the velocity given by the accelerating field—that is, there is here no indication of energy losses due to collisions. The slight drop which occurs at first in the curve and which is found at the beginning of all the curves is probably due to mercury vapor which it was impossible to completely eliminate from *e*. The slight rise which occurs just before the terminal drop has been accounted for as due to electron reflections from *e*. Such a curve gives the best direct evidence that we have of the elasticity of collisions below the resonating potential.

The next curve[1] with 5 (6) volts' accelerating potential was (for the fastest electrons) just above the resonating potential, and gives direct evidence of inelastic collisions involving an energy loss of approximately 4.9 volts. The slight drop at the left end of this curve is due to electrons suffering such collisions. The 6 (7)-volt curve also shows this same energy loss, in this case suffered by a much larger proportion of electrons. At all higher voltages a similar collision is evidenced. Beginning at 7 volts (corrected), however, there are indications of another type of collision with energy loss of 5.7 volts. And at 8.5 volts the expected collisions involving losses of 6.7 volts begin to occur, and become more pronounced at 9 volts. The next three curves are taken above the ioniza-

[1] Since the general shape of the curve was in some regions well known from previous work, and since it was desired to take these curves in as rapid succession as possible, the dashed portions were not actually observed.

tion point, and show the extreme importance of the 6.7-volt type of collision, the 4.9-volt and 5.7-volt drops having nearly disappeared. The 19-volt curve shows indications of an energy loss of 2 × 6.7 volts, corresponding to two of the more probable collisions.

The upper two curves of Fig. 4 were taken at higher vapor pressures, and show somewhat more pronounced drops at the critical potentials. The upper curve was taken just above the point at which ionization set in, and this shows that, at this voltage the 4.9 types of collision have become extremely improbable.

The 6.7-volt type of collision is then possible, and indeed above the ionization point is extremely probable as compared with the 4.9-volt collision. It does not seem to occur, however, in the cases of electrons with velocities only slightly in excess of 6.7 volts, but first occurs to an appreciable extent at 8.5 volts. The results are in exact accord with the hypothesis set forth earlier in the paper. That hypothesis was there seen to be required to explain the results of Mohler, Foote and Meggers; the present experiment is its direct proof. This completes the case for a 6.7-volt type of collision.

The distribution of velocities is more directly shown if the slope of the curves of Fig. 4 is taken and plotted as a function of the retarding potential. Such curves are given in Fig. 5. As in Fig. 4 the curves are super-

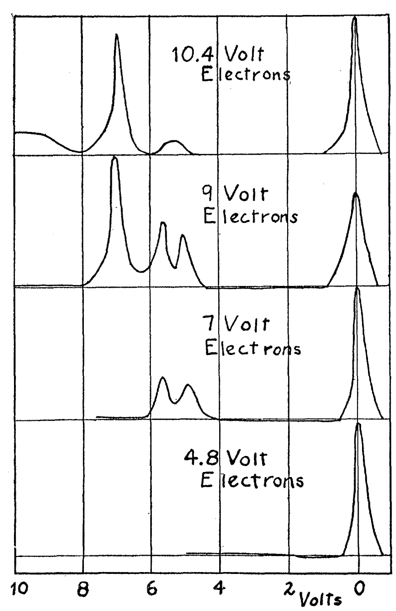

Fig. 5.

imposed and the scale of abscissas, instead of giving the retarding potential, gives directly the energy losses which have been suffered. The curves which are shown are for electrons which before collision had energies of 4.8, 7, 9, and 10.4 volts, respectively. The ordinate gives the relative number of electrons which have suffered energy losses corresponding to any particular value of the abscissa.[1] The negative values of the ordinates are of course meaningless, and are due, as mentioned above, to reflection from the walls of the receiving tube.

Comparison with Spectroscopic Data.

Mohler, Foote and Meggers obtained resonance curves for cadmium, zinc, magnesium, and calcium similar to that for mercury. In each of these cases, then, there are two types of inelastic collision, and in the cases of the first three metals their curves show that the conditions for the two types of inelastic collisions are similar to those which have been shown to exist for mecrury.

Corresponding to these types of inelastic collision, mercury, as is well known, has been found to give a single line spectrum λ 2536, which may be obtained with an impact potential of 5 volts. The line λ 1849 has never been observed below the ionization point, probably due to its strong absorption by the vapor. For three of the other metals both lines have been observed,[2] the line of shorter wave length first appearing in the case of zinc about 0.4 volt, in the case of cadmium about 0.7 volt, and in the case of magnesium 0.6 volt above the corresponding resonance potentials. This is in satisfactory agreement with the discovery of the second type of inelastic impact by Mohler, Foote and Meggers, and with the present investigation.

McLennan and Ireton have maintained that while the λ 2536 line is the more easily obtained by electronic bombardment, the series whose first member is λ 1849 is probably the one which corresponds to some very simple type of electronic vibration within the atom, and is more fundamental in character. This view is in accord with the present results which show that though the longer wave length is more readily excited at low voltages, at higher voltages it becomes quite insignificant in comparison with the radiation of the second type.

The results of Davis and Goucher, who found indications of strong photoelectric emission at 6.7 volts, and the more recent results of Franck

[1] While too much weight must not be laid upon the exact values of the ordinates the area under the peaks give the number of electrons which have suffered the corresponding energy losses.

[2] McLennan & Ireton, Phil. Mag., 36, p. 461 (1918); McLennan, Proc. Roy. Soc. A., 92, p. 574 (1916); Mohler, Foote & Meggers, Jour. Opt. Soc., 4, p. 364 (1920).

and Einsporn, who also detected this line among others, are not to be cleared up in this fashion. The methods employed by these writers gave the potentials at which the photoelectric emissions suddenly increased in value, and would be quite unable to detect the 6.7 type of emission if it did not begin until 8.5 volts.

In Goucher's curves we find a photoelectric effect beginning at 4.9 volts, which increases several fold between 6 and 7 volts, and a second quite sudden increase in the current at 9.8 volts. Perhaps these curves are not to be quantitatively explained. It is certainly difficult to see why, if the larger part of the photoelectric current just below 9.8 volts was due to 6.7-volt collisions, as the curves are interpreted to mean, so large an increase in current takes place at 9.8 volts which corresponds to two collisions of the 4.9-volt type.

Franck and Einsporn find curves having the same general shape as those of Davis and Goucher, but with large numbers of discontinuities in shape. These discontinuities, interpreted as spectrum lines, agree wonderfully well with prominent mercury lines. These lines have never been spectroscopically observed under these conditions. There are several difficulties which are met when we try to account for the shape of this curve, and the lack of proportionality between the magnitude of the photoelectric effect and the probability of inelastic impact is hard to explain—yet the checks found with spectral data are so striking as to make it almost impossible to doubt the interpretation. There remains, however, much to be done in correlating spectroscopic, photoelectric, and inelastic impact data, and it is not strange if the present experiment does not seem compatible with the photoelectric data.

Other Inelastic Potentials.

Two features of the present type of tube seemed to make it admirably fitted to detect other forms of inelastic collisions than those of the 4.9- and 6.7-volt type.

In the first place, the resolving power of this arrangement should be greater than of that hitherto employed. In the usual form of curve, the suddenness of the drop at a critical potential largely depends upon what function the probability of inelastic collisions is of the velocity. These collisions do not take place immediately as the critical potential is reached, but in increasing numbers as it is exceeded. This has just been shown to be strikingly true in the case of 6.7-volt collisions and for a considerable range of voltage seems true for the collisions at 4.9 volts. And equally serious is the fact that the recovery from such potential is not immediate but distorts the curve seriously for several volts after the potential has been passed.

The resolving power of the present arrangement, on the other hand, is conditioned only by the velocity distribution of the source. The accelerating potential may be placed at a value which will give the maximum number of collisions of the type desired, and the retarding potential will detect the number of such collisions present, the drop being completed in a range equal to the initial distribution. This distribution is, it is true, a serious matter, but it is hoped that this can be cut down to a small fraction of its present value.

In the second place, such a tube integrates the effects of the different types of collision, and so even though the initial potentials were too close to be observed separately, the presence of such potentials would be indicated by a gradual drop in the curve in that region. Assuming a perfect tube, the curve will be horizontal, except at such potentials.

It has already been seen that an inelastic collision appears to take place, involving an energy loss of about 5.7 volts. There is little evidence of still other types of inelastic collision. The region about 6.7 volts has been investigated with some care but no consistent inflections were found which could be attributed to other lines. The gradual downward slope of the curve in this region probably should be attributed to the imperfections of the method, and probably to the presence of mercury vapor in the supposedly evacuated region.

The drop at 5.7 volts is too pronounced to be disregarded, and to some extent supports the conclusions of Franck and Einsporn, who, it has been remarked, found strong indications of spectral lines and weaker evidence of inelastic collisions at 5.45 and 5.7 volts.

Turning again to spectroscopic observations, it will be recalled that the lines λ 2536 and λ 1849, corresponding to 4.9 and 6.7 volts' impact velocity, have been found to be absorption lines as was to be expected from the theory. A group of absorption lines has also been observed in the neighborhood of 2330, and also a line at 2140 Ångstroms.[1] No absorption lines other than these have been observed by McLennan and Edwards above 1849 Ångstroms. These wave lengths correspond to electron energies of 5.3 and 5.9 volts, respectively, and agree with the present observation of an energy loss in the neighborhood of 5.7 volts.

Collateral evidence for the existence of an inelastic collision in this neighborhood is furnished by resonance potential curves obtained by the writer some time ago, and which at that time were quite inexplicable, as in many features they still are. These curves (Fig. 6) resemble in many details one published by Mohler, Foote and Meggers. The peak

[1] Wood & Guthrie, Astro. Journ., 29, p. 211 (1909); McLennan & Edwards, Phil. Mag., 30, p. 295 (1915). McLennan & Edwards failed to find an absorption line at 2140, but it is not clear that this was not due to experimental difficulties.

appearing at 9 volts corresopnds to one which they attributed tentatively to λ 1435.6 or λ 1402.7. Interestingly enough, this curve shows a pro-

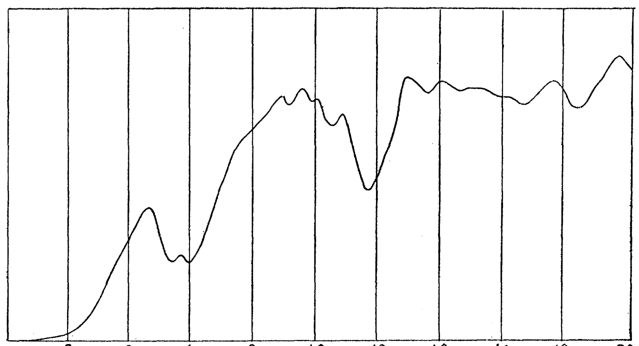

Fig. 6.

nounced maximum at 5.8 volts, which may be supposed to correspond to that placed at 5.7 volts from the velocity distribution curves.

Ionization.

In contradiction to the generally accepted belief concerning the phenomena taking place at the ionization point, the curves of Fig. 4 give no indication of a loss of 10.4 volts of energy. No evidence for such a loss exists elsewhere.[1] The 10.4-volt inflection in the usual form of ionization curve which indicates ionization, does not reoccur at 20.8 volts, and it has been suggested elsewhere that this may mean that ionization does not involve a loss of a definite amount of energy in the same manner that a resonating collision does. The absence of the inflection at 20.8 volts cannot be considered conclusive evidence in the matter, however, as the experimental conditions make it quite likely that the double collisions necessary to give this inflection would be very improbable, and if occurring be difficult to detect.

It would be quite in accord with the Bohr theory if energy was absorbed above the ionization point in any amount above that just required for ionization. As long as the excited electron stays attached to the atom, its energy absorption is definitely fixed by the energy of an initial and a final position. But a free electron may have any velocity, and so it is quite in line with the theory that a 19-volt electron, say, should lose any part or all of its energy; if it lost all of its energy, the emitted electron would have $19 - 10.4 = 8.6$ volts of energy after emission, and this

[1] Except some recent results, as yet unpublished, of Noyes and Gibson, which seem to indicate that such a loss does occur.

effect would be indistinguishable from the case in which the primary electron lost 10.4 volts and the secondary electron had zero velocity; if it loses energy in any random amount over 10.4 volts, the emitted electron must, by this accepted theory, have enough to make the sum of the two remanent energies 8.6 volts. The first case leads us to expect a sudden drop in the curve at 10.4 volts from the terminus, and another at zero retarding potential. The second case would be shown by a curve which gradually drops in the region from zero to 8.6 volts retarding potentials, and at 8.6 volts (with a perfect tube) becomes horizontal, or at least has a change in slope at this point. Neither is in accord with the results of this experiment. It is true that, though the curves do not have the change in slope we should expect at the ionizing point on the curves, they do have a continued drop, which has been accounted for by the presence of mercury in the region from *c* to *e*. It is possible that this is rather the effect for which we are looking, the drop being continued below the ionizing point by a miscellany of critical potentials in that region which have not been resolved.

To test this very important point, another tube was designed with a view to more immediate removal of the mercury which passes through the holes, to eliminate as far as possible the reflection of electrons, and to make it possible to check the behavior of the tube by taking conventional ionization curves. This is the tube which has been described (Fig. 3). The observations discussed in the above sections have all been checked with this tube.

It has been possible, under suitable conditions, with this tube to obtain curves which were practically horizontal except at the critical potentials. The upper curve of Fig. 7 is a typical velocity distribution

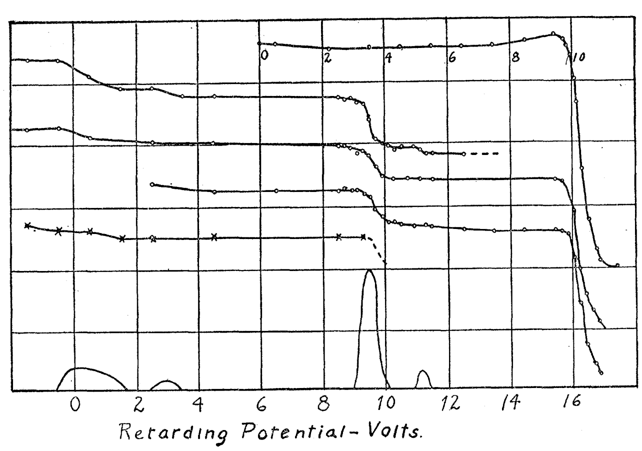

Fig. 7.

curve in vacuum. The other curves are for 16.5-volt electrons with the mercury at 90°. The cylinders *d* and *e* had been heated for some hours to drive out mercury as far as possible; during the observations they were cold.

By taking ionization curves by the usual method, measuring the current to *f*, it was ascertained that strong ionization was taking place under these conditions.

Several curves were taken with a view to detecting energy losses greater than 6.7 volts and these are given in the figure, with the current plotted against the retarding potential. From one of these curves (the upper one) the slopes have been taken and the lowest curve of the figure shows these slopes plotted as a function of the retarding potential. The curves all drop during the first volt; and two of the curves show another slight drop at about 3 volts. The current then remains constant until a retarding potential of about 9 volts is reached, when a drop occurs which is due to electrons which have made a 6.7-volt collision. A much smaller drop occurs at 11 volts, attributable to collisions of the 4.9-volt type. The drop which occurs in two of the curves at about 3 volts can be accounted for as due to two collisions of the 6.7-volt type. Between 3 and 9 volts the curves show no decrease in the current with increasing retarding potential and so are in contradiction both with the view that a loss of exactly 10.4 volts occurs at ionization and that a loss of energy in random amounts above this value can occur, with a transfer of the excess over that needed for ionization to the secondary electron. The first view would lead us to expect a sudden drop in the curve between 5.5 and 6.5 volts; from the second we would expect a gradual decrease in current in the region from 0 to 6 volts' retarding potential.

On all of the curves a slight drop is to be observed with small retarding potentials (1 volt) and the same effect is seen in curve 11 (12) of Fig. 4. This indicates a number of very slow electrons present after collision. It is not to be expected that these current drops will be large, because the slow electrons which are here being measured will quite likely combine with the positive ions present before they reach the hole in *c*. However, if *c*, *d*, and *e* are given a slight accelerating potential with respect to *b* ($\frac{1}{4}$ volt), we should expect to get more of them, and in fact it is observed that under these conditions the current to *e* is greatly increased, perhaps twenty-fold. The current is reduced to its normal value, unless *e* is slightly accelerating. Such a phenomenon is only to be observed with accelerating potentials sufficient for ionization. This shows that there are indeed present at ionization a large number of electrons with zero velocity. Whether such electrons are the primary ones from the cathode, or those released at ionization, cannot be directly determined. However, since Fig. 7 shows that a total loss is the only loss greater than 6.7 volts which occurs, we may suppose that both primary and secondary electrons are represented in this group; that is, that after an ionizing collision, both primary and secondary electrons have zero velocity.

This conclusion seems to disagree with the Bohr theory, but perhaps this disagreement is not insuperable. Immediately after the removal of an electron from the atom it is conceivable that the remaining electrons do not have stable configurations and are quite easily displaced. Possibly after the electron strikes the atom and removes one electron, it may use its remaining energy in displacing other electrons in the now less stable ion. If the conclusion drawn from the experiment is to be accepted as valid, by some such picture as this it is possible to remove the discord with the Bohr theory.

Professor Wood [1] has found that above the limit of the principal series, the light absorption of a vapor becomes continuous. Such light should produce ionization, and this has indeed been shown to be the case in an investigation which has just been completed by R. C. Williamson. This continuous absorption of light for frequencies greater than the limit of the principal series presents an obvious parallel to the continuous absorption of energy of the electron when its energy is above the ionizing potential. It is a very interesting question whether the emitted electron in this photoelectric ionization has an energy at emission corresponding through the $h\nu$ relation to the amount by which the frequency of absorbed light exceeds the limiting frequency of the principal series. Such has been our general view, but if the parallel with the present results is perfect, these emitted electrons should have a zero velocity.

Conclusions.

The principal results which have been obtained from an examination of the residual energies after collisions of electrons in mercury vapor are:

1. The discovery by Mohler, Foote and Meggers of a resonance potential involving an energy loss of 6.7 volts has been confirmed. It has been shown that while this collision does not occur below 8.5 volts, at voltages above the ionizing point, this type of collision attains overwhelming importance in comparison with the collisions of the 4.9-volt type.

2. It is probable that inelastic collisions involving an energy loss of about 5.7 volts also occur, checking, to this extent, with the conclusions of Franck and Einsporn. The absorption lines which have been found

[1] Phil. Mag., 18, p. 531 (1909).

in the spectrum of mercury support this view. Inelastic collisions corresponding to the other photoelectric lines of Franck and Einsporn have not been found.

3. At ionization the electron loses its total energy, even though this much exceeds the ionizing potential. The electron which is the product of the ionization seems likewise to have a negligible energy.

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