ELECTRON ENERGY LOSSES IN MERCURY VAPOR

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Abstract

An improved magnetic spectrum method was used to determine the energy losses sustained by slow speed electrons in mercury vapor. Electron energies up to 60 volts were used, the main region of interest being from 0 to 25 volts. The energy losses detected, below that required for ionization, were; 4.9, 5.4, 6.7, 7.7, 8.8, 9.8 volts. These correspond to practically all the transitions of a valence electron from the basic $1S$ level up to each of the higher levels to $4P$. No evidence of other losses such as are observed by the photoelectric method were found. At voltages above 10.4, the ionization potential, electrons seem to be able to give up any quantity of energy in excess of that required for ionization, the higher losses being favored. A very interesting loss of 11.07 volts has been found, which has not been recorded heretofore. It begins to be resolved at about 18 volts, and grows steadily with increasing voltage in much the same manner as the 6.7 volt loss. It is thought that this loss involves the simultaneous displacement of both valence electrons from their normal levels.

THE pioneer work on inelastic impacts of electrons with mercury atoms, by Franck and Hertz,[1] showed that the energy lost by the electron is quantized. At first there appeared to be but one type of inelastic impact, that in which the loss of energy was equivalent to a drop in potential of 4.9 volts. Since that time, three other types of losses have been found by this or similar methods.[2,3,4] The photoelectric method, developed by Franck and Einsporn,[5] is also capable of giving us an insight into the phenomena of impacts. The number of critical potentials found by this latter method is quite large —eighteen, in the work referred to, and a still larger number in the later work of Jarvis.[6] Some of these critical potentials have been shown [7,8] to be due to other effects than resonance collisions: but there has persisted a discrepancy between the results of each of these methods, not only with each other, but with the results of spectroscopic study.[9,10,11,12,13]

[1] Franck and Hertz, Verh. d. Deut. Phys. Ges. **16**, 457 (1914).
[2] Mohler, Foote, and Meggers, Phys. Rev. **10**, 101 (1917).
[3] Eldridge, Phys. Rev. **20**, 456 (1922).
[4] Whitney, Phys. Rev. **34**, 923 (1929).
[5] Franck and Einsporn, Zeits. f. Physik **2**, 18 (1920).
[6] Jarvis, Phys. Rev. **27**, 808 (1926).
[7] Webb, Phys. Rev. **24**, 113 (1924).
[8] Messenger, Phys. Rev. **28**, 962 (1926).
[9] Hertz, Naturwissenschaften **11**, 778 (1923).
[10] Eldridge, Phys. Rev. **23**, 685 (1924).
[11] White, Phys. Rev. **28**, 1125 (1926).
[12] Valasek, Phys. Rev. **29**, 817 (1927).
[13] Crozier, Phys. Rev. **31**, 800 (1928).

It seemed highly desirable that the inelastic impact method, which, in the past, has given the most meager results, should be improved, with a view to determining which of the impacts involve actual quantized energy losses to the electrons. For this purpose, the method used by Whitney[4] has certain points of advantage over other methods. The electrons which have lost energy are spread out into a velocity spectrum, and can be collected, group by group, without mutual interference. This makes possible the use of greater sensitivity, in the search for the less probable types of losses. While Whitney was primarily interested in the excitation functions of the more probable impacts, his failure, under apparently favorable conditions, to detect the losses observed by the photoelectric method increased the difficulty of a reconciliation between results of the two methods.

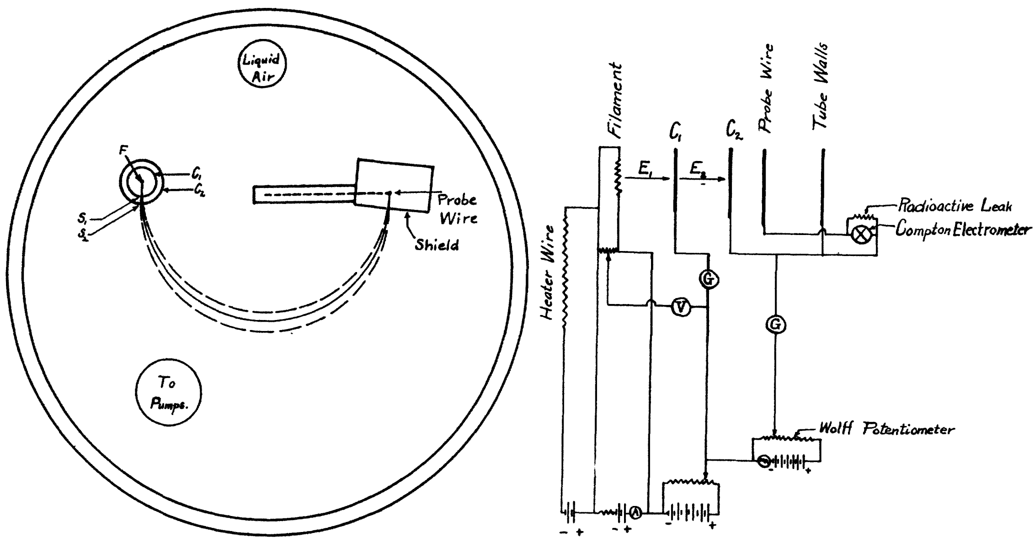
A possible explanation of this discrepancy, as Whitney points out, would be that the types of losses which he does not find, are very improbable, except when the electron has little more than the amount of energy required for the excitation. Since Whitney's apparatus was quite insensitive to very slow electrons, we can see how these collisions involving a total loss of energy, would, under this hypothesis, have escaped detection. We therefore set about to remove this limitation by increasing the sensitivity of the Whitney method for slow speed electrons, and at the same time, to improve the resolving power. An additional end has been gained by a change of procedure which allows the energy losses to be read directly in volts from an accurate potentiometer, rather than by means of a calibration curve.

Apparatus

The apparatus is pictured in Figs. 1 and 2. Electrons evaporating from the unthoriated tungsten filament F, are attracted toward the concentric cylinder C_1, during which time they may make elastic or inelastic impacts with the atoms of mercury vapor which fills this region. A sample of the electrons arriving at the cylinder pass through the slit S_1. The second cylinder, C_2, allows us to control the speed with which the electrons emerge from S_2. In the electric field free region outside the cylinders, the electrons are spread into a velocity spectrum by means of a uniform transverse magnetic field produced by a large pair of Helmholtz coils. Electrons having some definite speed, determined by the strength of the magnetic field used, will converge at a point 180° distant from S_1, along an arc of a circle of 5 cm radius. Here they are collected by a probe wire which is shielded from stray electrons. A Compton quadrant electrometer, shunted by a radioactive leak, measures the current to the probe, which is of the order of 10^{-11} amp.

The vacuum tube was made entirely of brass, 3/8″ thick, 20 cm diameter, and 22 cm long. The only metal parts of other material were the inner (molybdenum) cylinder and the tungsten filament. Two small glass windows and a reentrant liquid air trap, used in freezing out the mercury vapor from the outside region, were carefully shielded with brass wire gauze. The vacuum was kept below 10^{-5} mm, and liquid air traps employed constantly. The mercury vapor was introduced into the impact chamber from a furnace heated reservoir maintained at various temperatures from 90° to 118°, depending on the pressure desired. The vapor pressure, under these conditions, is hard to estimate, since diffusion through the slit S_1 and the temperature of the impact chamber play an uncertain role; from the probability of certain types of losses, the pressure seemed to be of the order of 0.1 mm.

While a number of changes have been made, the tube, as described above, is essentially of the same type as that employed by Whitney. The chief point of difference lies in the addition of the auxiliary accelerating cylinder, C_2. By means of this cylinder, the speed of the electrons may be adjusted so that any particular group may be focused on the probe wire, without changing the magnetic field.



Figs. 1 and 2. Plan of apparatus and electrical circuit.

Procedure

In Whitney's method, the electrons emerging from C_1 with various residual speeds, were collected, group by group, by varying the magnetic field. In the present work, the procedure was somewhat different. All of the electrons collected were made to travel the circular path to the probe, with the same speed, regardless of how much energy they had lost. This was accomplished by accelerating them enough between C_1 and C_2 to just make up for their loss in energy at impact. For example, the 6 volt curve in Fig. 4 was taken as follows. E_1, the potential on C_1, was set at 6 volts, the desired impact speed. E_2, the difference of potential between C_2 and C_1, was set at (say) 2 volts. The magnetic field was then adjusted for maximum probe current, i.e., for 8 volt electrons. E_2 was then varied from 0 to 8 volts, in convenient steps of, generally, 0.1 volt, and the data recorded directly on graph paper. Those electrons which have lost none of their initial 6 volts, will require but two volts to be brought to the probe wire: but those which have lost 4.9 volts at an inelastic impact, will require that much more energy, or a total of 6.9 volts acceleration between the cylinders, in order to have the proper speed to be collected. The no-loss electrons then have, of course, 10.9 volts, and hence move in too large a circle to interfere. If the arbitrary two volt initial value of E_2 be neglected in plotting, the abscissas of the peaks give the values of the energy losses directly in volts, and the ordinates, approximately the relative probability of each type of impact, at a particular impact speed. The width of the peaks is due to several causes, such as velocity distribution in the original electron stream, imperfect focusing, and finite width of probe.

Fig. 3 shows the degree to which this method was successful in improving the sensitivity for slow speed electrons. The first curve is similar to that

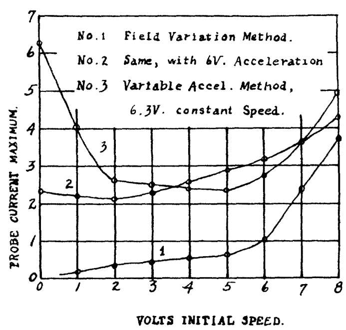


Fig. 3. Efficiency of collection of electrons as a function of their voltage.

published by Whitney, and shows the efficiency of collection of electrons, in the absence of the auxiliary cylinder. Curve 2 shows that, when this cylinder is inserted and maintained at a potential 6 volts above that of the first cylinder, the slow electrons are collected much better than before. In making curve 3, the new method of procedure was used. The total speed of collection was always 6.3 volts, but the speed with which they emerged from S_1 is varied from 0 upward. Slow electrons are still more favored than in the preceding curve, but the direct-reading characteristic of the new method is an additional advantage.

Results

Fig. 4 shows the type of curves that are obtained with electron energies below ionization. The 4.9 volt loss, which is the predominant one up to 9 volts, begins to show itself at as low as 4 volts. In that curve, it appears to be a loss of only 4.3 volts, rather than 4.9 volts. These two illusions, the detection of a loss at too low a voltage, and the apparent smallness of the loss are traceable to the rather large velocity distribution—amounting to about 1.6 V.—which is here present. Since the potential E_1 is measured with respect to the center of the emitting portion of the filament, a certain share of the electrons may well have enough more energy than the average, to be able to lose 4.86 V. After this loss, a subsequent addition of less than 4.86 V. would be required in order to collect them at the normal speed. This effect is most prominent for the types of losses which increase most rapidly in the vicinity of their critical potentials. The occurrence of a loss by an electron which apparently does not have that much energy might also be due to impacts occurring between the two cylinders, after the electron has acquired part of the added potential E_2, though this is not considered likely.

At an impressed voltage of 5.2, an energy loss of 5.4 V. is clearly discernible, anticipated in voltage for the same reason as in the case of 4.9. A 6.7 V. loss is seen in the 6.5 volt curve, anticipated less than 4.9 was, and probably less than 5.4 would have been, had the latter not been partly obscured by the 4.9 V. peak.

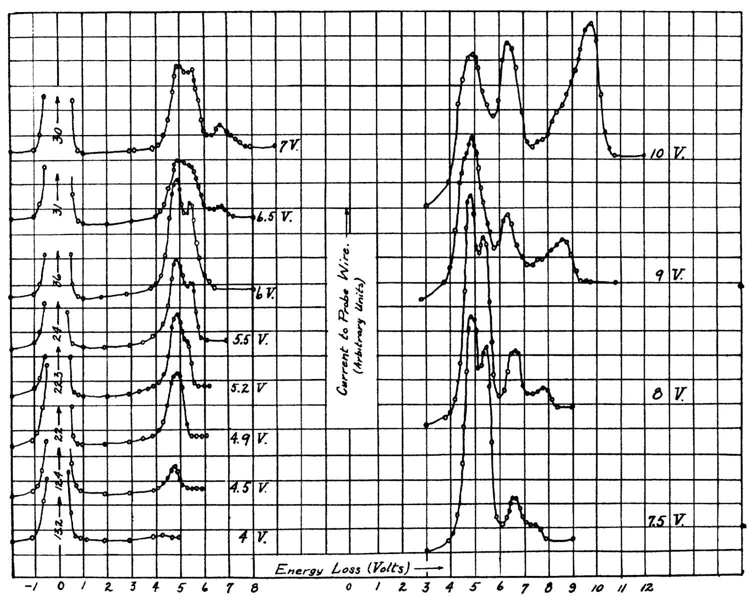


Fig. 4. Energy losses in Hg below ionization.

The failure of previous users of the inelastic impact method, to find a loss of 7.7 V., or 7.9 V., corresponding to transitions of the valence electron from the $1S$ to the $2s$ or $2S$ levels, has been a serious criticism of the completeness of the results to be obtained by this method. These levels are separated by approximately a volt on either side, from all other levels, and upward transitions to them should be easily observable, if their probability is at all large. That such a loss does occur is seen from the curves of Fig. 4, beginning with the one for 7.5 V. The probability of the loss, while always small, rises to a maximum and falls off to insignificance within two or three volts of its critical potential. The exact loss could not be determined with much accuracy, but appears to be 7.7 V., though 7.9 might also be present. It is interesting to note that Crozier[13] found that the intensity of the downward transitions from

$2s$ to $2p_{2,3}$, changed in a similar manner, while transitions from $2S$ had but one-third the probability in comparison.

The well-known loss of 8.8 V., and a loss of 9.8 V., sometimes observed, but attributed to two successive 4.9 V. losses, complete the list of losses less than that required for ionization. These may be seen better in Fig. 5, at impact speeds above ionization, because of their increased probabilities of occurrence. At 41 V., the 9.8 V. peak is at least as large as the single 4.9 V. peak, while the multiple collision peaks involving one or more 6.7 V. loss, are, quite properly, but a small fraction of the size of the single loss peak. This

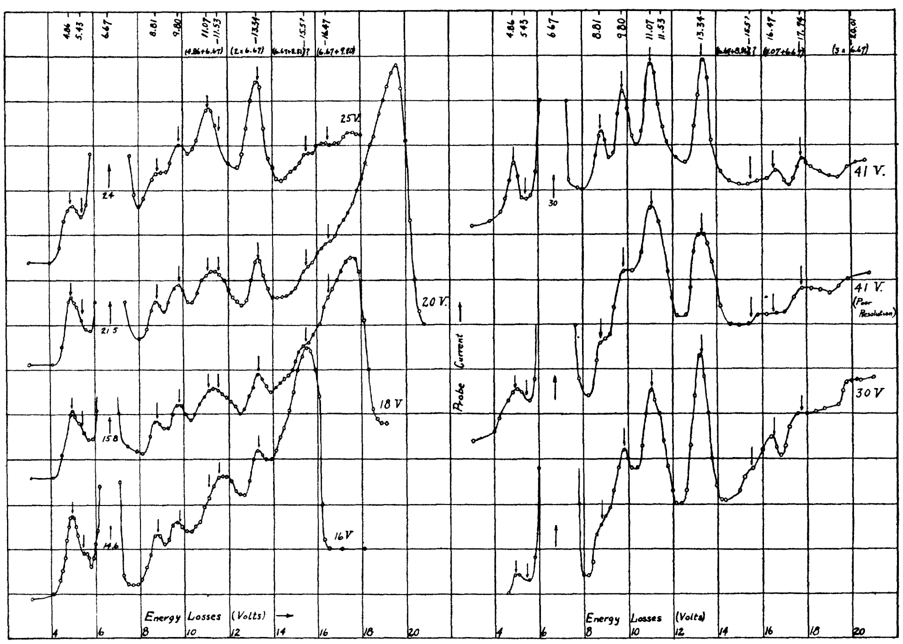


Fig. 5. Energy losses in Hg at higher electron voltages.

consideration, along with a study of the change of size of the 9.8 V. loss with change of vapor pressure, leaves little doubt of its interpretation as a single impact loss.

Ionization

In all the curves taken with impact speeds above about 10 V., the threshold current, upon which the inelastic impact peaks are superimposed, rises rapidly in the vicinity of the region indicating total energy loss. It falls again, of course, at a distance beyond the total loss value, equal to half the velocity distribution. In other words, this rather large group of electrons appears to lose any amount of their energy from about that required for ionization up to total loss, the great bulk of them being in the latter category. The absolute number of these electrons is probably a great deal less than would be inferred from the size of the peak, because of the facility of collection of slow electrons, as previously explained. It was suspected that these slow electrons might have lost their energy at reflection from the walls of one of the cylinders. To test this, the furnace was cooled to 25°C, when the slow speed peak persisted to a certain extent, while the inelastic impact peaks practically vanished. The conclusion derived from this was that a part of the effect was due to reflected electrons from the cylinder walls, but that the major portion was to be attributed to some kind of a loss involving the mercury vapor, presumably associated with ionization. Eldridge[3] came to the conclusion that, at ionization, both the impacting electron and the electron born of ionization had but a negligible amount of energy. What to do with the extra loss of energy is a moot question. Some later authors have supposed a sharing of the surplus energy by the two electrons: on this hypothesis, the current due to this source should be symmetrical about a line midway between total loss and ionizing loss; this is decidedly a different distribution than that observed here. This is, admittedly, an unsatisfactory way to leave the problem, but additional information is needed before a better interpretation can be made by this method.

Energy Losses Above Ionization

When relatively high potentials are being used, and the losses under investigation are but a fraction of the total electron energy, it becomes very advantageous to be able to use a retarding potential between the two cylinders C_1 and C_2, rather than an accelerating one, as was described in the investigation of losses near their critical potentials. Consider, for instance, the two curves in Fig. 5, marked 41 V. The upper curve was taken with a magnetic field set to collect 15.1 V. electrons to the probe wire. In order to collect the electrons which have lost no energy at impact, a retarding potential of 25.9 V. must be applied between the cylinders. As this retarding potential is reduced, which is equivalent to *increasing* the *accelerating* potential in the previous cases, electrons which have lost more and more energy are brought into focus and measured. This results in a controllable increase in the percent separation of the groups of electrons, with an accompanying increase in resolving power which is very desirable. The lower 41 V. curve was taken with a field set for 27.2 V. electrons, and hence with less retarding potential. The one-volt separation between the 8.8 and 9.8 V. losses is now but one-half the fraction of the whole path speed that it was before, and the peaks are no longer separated. With no retarding potential, the resolution was extremely bad. This improvement in resolution has been accomplished at the sacrifice of fidelity in the measurement of probabilities, in which we are not so much concerned in the present paper.

The chief point of interest in the curves of Fig. 5, is the 11.07 V. loss, which is seen to rise to an importance second only to that of the 6.7 V. loss, at this voltage. Its value may be observed very accurately, due to the presence of peaks of known value on either side of it, so that the value given is probably accurate to within 0.03 V. It makes its appearance at a potential unfavorable to its detection, because of the presence of the peak due to the double impact loss 4.9+6.7. Rising steadily from about 18 V., where the masking peak drops rapidly, this loss becomes so prominent that, at 41 V., we even see a peak due to the double impact 11.07+6.67.

Several possible interpretations for this type of energy loss have been studied. No combination of the known losses in either the arc or the spark systems would give this value. Moreover, when the vapor pressure is changed, the size of the peak remains proportional to the single impact peaks rather than to the double impact peaks, which decrease more rapidly. It is therefore thought to involve but a single impact. If this were a *critical potential* method, a delay in the appearance of the loss until the energy of impact was somewhat above the amount required for ionization, might be interpreted as a delay in the process of ionization until some conservative force be overcome: but here, we are measuring the actual amount of the energy lost by the electron, regardless of the total energy possessed. Hence, some other type of quantized loss would have to accompany ionization, in order to account for the excess energy. According to the HgII energy values of Carroll,[14] the simultaneous ionization and spark excitation to the lowest level would involve 16.8 V. Even then, it is doubtful whether the loss would be quantized, because of the possibility of energy sharing by the two electrons, as in ordinary ionization.

The most likely interpretation so far found, seems to be that of simultaneous excitation of both valence electrons in the same atom, without ejection of either. So little is known concerning this interesting type of excitation, that a complete verification of this theory is not to be expected at this time. Sawyer[15] has classified four lines in mercury, which he attributes to such double transitions, and from them, arrives at the values of the three lowest "p'" levels.[16,17] The lowest of these has a wave number of -7860 (negative, because it lies above the ionization level), so that excitation to this level $(1S-p_3')$ would require 11.35 V. This is 0.28 V. more than that found in the present work, which is far too great a difference to be attributed to experimental error in either method. Sawyer points out, however, that this level was determined by a single line, which might have a different interpretation; the other, and higher levels have as many as three transitions observable, and hence are much less in doubt. It is possible that a reclassification of these lines, with a lower level in mind, might bring about a better agreement.

Conclusions

The energy losses observed in this work are; 4.9, 5.4, 6.7, 7.7, 8.8, 9.8, and 11.07 V.—all save the last named one being those predicted on spectroscopic grounds. The circumstances of the appearance of 7.7 both increase confidence in the data given by the inelastic impact method, and explain the

[14] Carroll, Phil. Trans. **225,** 357, A 634 (1926).
[15] Sawyer, J.O.S.A. **13,** 432 (1926). For pioneer work on p' levels see thefollowing articles.
[16] Wentzel, Phys. Zeits. **24,** 106 (1923); **25,** 182 (1924).
[17] Russell and Saunders, Astrophys. J. **61,** 8 (1925).

difficulty of detection of certain losses. Failure to detect 4.7 V. losses is attributed to the extremely large probability and rapid rise of the 4.9 V. loss, together with a rather large velocity distribution. Excitation to the $3S$ and to all of the "4" levels, involving about 9.2 and 9.5 V. losses, are thought to be even less probable than 7.7 V., and hence not detected. The unexplained losses of the photoelectric method were not observed, although they should have been, had they represented actual quantized losses of electronic energy of any appreciable probability. The energy loss at ionization is not quantized. The new loss, of 11.07 V., is thought to represent new data opening up the question of p' energy levels and simultaneous excitation of two valence electrons. The present method has not yielded spark terms, but may do so, if ionization be accomplished prior to the excitation dealt with here.

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