running in parallel with the apparent simple changes of density of the imprisoned air. I have not succeeded in fully searching it out; but the evidence so far obtained points to the heat produced on turning the stopcock as the source of the discrepancy. It is improbable, of course, that small increments of the expansions and the compressions of a gas should not be symmetric.

* These PROCEEDINGS, 15, 1929, 22-25.

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ON ELECTRONS THAT ARE "PULLED OUT" FROM METALS

By Edwin H. Hall

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Communicated February 7, 1929

The work\(^1\) done by Millikan and his co-laborers, Eyring and Lauritsen, on the subject of "pulling" electrons out of metals has attracted much well-merited attention, but in the present paper I shall undertake to discuss certain aspects of this matter which I have not seen presented in print.

It is well known, to the editor of these PROCEEDINGS at least, that I am the somewhat persistent advocate of the proposition that we can best explain the phenomena of conduction, of thermoelectric action and of the Volta effect in metals by supposing that the electrons taking part in these phenomena are of two classes, the classes differing from each other in respect to the mean kinetic energy and mean potential energy of the individual electrons composing them.

The electrons of one class are supposed to be in a state of higher potential energy than those of the other class and to share the energy of thermal agitation proper to the temperature of the metal. These I usually call the "free" electrons, but I shall in this paper, adopting the name used by Millikan, call them "thermions." Conduction electrons of the other class are not supposed to share the energy of thermal agitation, being less free from atomic union than the others, and I have usually called them the "associated" electrons. I shall in this paper call them "valence electrons."

I have been gradually coming to the conclusion that the thermions are very few\(^2\) compared with the atoms, a conclusion that receives some support from the experimental evidence offered by F. Evelyn Colpitts in a recently published paper.\(^3\) I shall refer to this matter again further on.

Years ago I inferred from conduction and thermo-electric data that in
most metals the thermions carry a much smaller fraction of the current than do the other class of conduction electrons. For example, I estimated\(^4\) that in tungsten at 0°C., the thermions are to be credited with only about 4% of the current.

The conclusions drawn from their experiments by Millikan and Eyring were in some respects strikingly similar to those indicated above. In the abstract of their paper they say, "'The lack of dependence of field currents upon temperature furnishes strong evidence that most of the conduction electrons do not share in the energy of thermal agitation. The thermions, however, do share in this energy; they are presumably responsible for the Peltier and thermo-electric effects.'"

I called attention\(^6\) to this similarity of views soon after the paper just referred to appeared, but in one respect, apparently, similarity was lacking. I have not detected in the paper of Millikan and Eyring or in that of Millikan and Lauritsen any indication of an opinion that the two classes of conduction electrons are in different states of potential energy, implying different amounts of work against opposing forces required to remove them from the metal. My own theory, on the other hand, assumes such a difference of potential energy.

I write as the amount of energy required to bring a conduction electron from the non-thermal state to the thermion state

\[
\lambda' = \lambda'_c + sRT,
\]

where \(\lambda'_c\) and \(s\) are constants and \(R\) is the gas-constant for a single atom. At room temperature and thereabout \(\lambda'_c\) is for most metals much smaller than \(sRT\). Thus when \(\lambda'\) is expressed in ergs, \(\lambda'_c\) is for tungsten taken as \(40 \times 10^{-16}\), while \(s\) is taken as 11.4 and \(R = 1.37 \times 10^{-16}\). I have no great confidence in the accuracy of the values assigned to \(\lambda'_c\) and \(s\), and there is risk in extending the application of equation (1) to high temperatures, but taking this risk we get for tungsten the following values of \(\lambda'\):

<table>
<thead>
<tr>
<th>(T) (in K)</th>
<th>(\lambda') (in ergs)</th>
<th>(\lambda') (in electron-volts)</th>
</tr>
</thead>
<tbody>
<tr>
<td>300 K</td>
<td>(4.7 \times 10^{-16})</td>
<td>0.30</td>
</tr>
<tr>
<td>600 K</td>
<td>(9.4 \times 10^{-14})</td>
<td>0.59</td>
</tr>
<tr>
<td>900 K</td>
<td>(14.1 \times 10^{-14})</td>
<td>0.89</td>
</tr>
<tr>
<td>1000 K</td>
<td>(15.7 \times 10^{-14})</td>
<td>0.99</td>
</tr>
<tr>
<td>1100 K</td>
<td>(17.2 \times 10^{-14})</td>
<td>1.08</td>
</tr>
<tr>
<td>1200 K</td>
<td>(18.7 \times 10^{-14})</td>
<td>1.18</td>
</tr>
</tbody>
</table>

From my point of view the value of \(\lambda'\) measures the advantage which a thermion has, compared with a conduction electron of the other class (a "valence" electron), in the operation of escape from the metal. If thermions and valence electrons were equally numerous within the metal, the thermions would furnish more than half of the field current,
and the field current, for a given strength of field, would be a function of temperature. The same general proposition would hold, of course, if \( \lambda' \) represented merely the energy inherent in the gaseous state of the thermions. The fact that below 1100\(^\circ\)K., and with fields not above a certain strength, no such dependence upon temperature was indicated, in the experiments of Millikan and Eyring, was doubtless their reason for concluding that the thermions are few compared with the other conduction electrons.

The main purpose of the following discussion is to find, as definitely as possible, how few the thermions must be, compared with the valence electrons or with the atoms, in order with my values of \( \lambda' \) to contribute so little to the field current as the experiments of Millikan and Eyring would indicate.

I shall not be disturbed if I find the thermions relatively very few. In a paper already referred to (in footnote 2), applying my ideas to the emission data furnished by Dushman and his co-workers, I have obtained the following tentative expression for \( n \), the number of thermions per cu.-cm., in thoriated tungsten:

\[
n = 3.86 \times 10^{11} \times T^{1.48}. \tag{2}
\]

Taking \( N \), the number of atoms per cu.-cm. in tungsten, as \( 6.3 \times 10^{22} \), I get by use of (2) the following estimates:

<table>
<thead>
<tr>
<th>( T ) (^\circ)K.</th>
<th>( n ) ( \times 10^{14} )</th>
<th>( N + n ) ( \times 10^{4} )</th>
</tr>
</thead>
<tbody>
<tr>
<td>300</td>
<td>1.8</td>
<td>35</td>
</tr>
<tr>
<td>900</td>
<td>5.0</td>
<td>13</td>
</tr>
<tr>
<td>1100</td>
<td>12.2</td>
<td>5</td>
</tr>
</tbody>
</table>

Miss Colpitts, in the paper already referred to, made use of a method having no relation to thermionic emission. Working at room temperature she found that her experiments indicated for one tungsten film \( n = 1.4 \times 10^{15} \) and for the other tungsten film \( n > 9.2 \times 10^{15} \), and so of course the conclusion to be drawn is somewhat doubtful; but, taken as a whole, the evidence she presents is not unfavorable to the view that the estimates which I have given above are of the right order of magnitude, and this is all I can claim for them at the best.

In dealing with the experimental data furnished by the papers of Millikan and his co-workers I shall make much use of certain conclusions arrived at by Dr. J. R. Oppenheimer, who has applied the ideas and methods of wave-mechanics to the phenomena in question. He remarks, "Any field, no matter how weak, will in time dissociate an atom. This is essentially a consequence of the fact that the motion of the electron is no longer absolutely restricted to a region of the dimensions of the Bohr
orbit; it will now occasionally, though not very often, be found at points much further from the nucleus; and the further it is, the smaller will be the field required to insure that it does not return to the nucleus. Since the probability that an electron be at a distance \( R \) from the nucleus falls off exponentially with increasing \( R \), the rate at which the field ionizes the atom may be expected to decrease rapidly when the field strength is decreased." Presently he gives an expression, numbered (1), for the rate at which a "hydrogenic atom with ionizing potential \( W \)" dissociates under the influence of a field \( F \). This expression begins with a numerical factor, and this observation is made: "If the wave-functions of the atom are not quite hydrogenic in character, . . . the numerical factor may vary by a factor, perhaps, of two."

In Oppenheimer's expression (1) \( W \) is taken in ergs, while \( F \) and the electron charge \( e \) are taken in e.s.u.; but later \( W \) is expressed in electron-volts and \( F \) in volts per cm. With this understanding we have the following statement: "The formula (1) gives in amperes for the current per series electron:

\[
i = 3 \times 10^{-8} F^{1/4} W^{1/4} \exp\left(-10^8 \frac{W}{F^1}\right).
\]

By "series electron" I understand, after consultation with younger colleagues, "valence electron." For tungsten, the metal used in the experiments under consideration, there are six valence electrons per atom.

Going over carefully the steps needed to proceed from expression (1) to equation (3) I have been unable to verify the two constants \( 3 \times 10^{-8} \) and \( 10^8 \) given by Oppenheimer in this equation. I get this

\[
i = 72 \times 10^{-8} F^{1/4} W^{1/4} \exp\left(-6.85 \times 10^7 \frac{W}{F^1}\right),
\]

and my values of the constants have been verified by my colleagues, Professor Kemble and Dr. Guillemin. I have made no attempt to allow for the departure of the tungsten atom from the hydrogenic type, understanding from Dr. Oppenheimer's statement, quoted above, that this consideration would account for no great variation of the initial numerical factor in (3).

It is to be noted that \( W \) means the work done against opposing forces in taking a valence electron from the surface layer of atoms out into the space surrounding the metal, beyond the reach of the metal's attraction. Oppenheimer, whose paper is dated from the Norman Bridge Laboratory at Pasadena, and who doubtless had all the data there available at his command, gives 4.7 as an estimate of the value of \( W_e \) in electron-volts. The process by which this estimate was made is not fully shown, and probably no great accuracy would be claimed for this particular value
of \( W \). But Warner\(^7\) gives 4.79 volts as the "photo-electric work-function" for tungsten, and Dushman\(^8\) gives to the constant \( b_0 \) in Richardson's therionic emission equation a value which indicates a work-function of 4.51 volts for tungsten. There is a strong tendency\(^9\) now to identify the volt-equivalent of \( b_0 \) with the photo-electric work-function, and so we can take Warner's 4.79 and Dushman's 4.51 as estimates of the same quantity as that denoted by Oppenheimer's \( W \). The value 4.7 is near enough to the mean of the three estimates, and I shall use this value, taking it as a constant independent of temperature.

The \( F \) of Millikan and Eyring's paper is calculated in a purely conventional way, by means of the rule

\[
F = 228\phi
\]

"where \( \phi \) is the difference in potential between the electrodes"; that is, between the emitting thoriated tungsten wire and the receiving copper cylinder which surrounded it. The diameter of the wire was 0.00123 cm., that of the copper cylinder was 1.625 cm. \( F \) was intended to be the field strength at the surface of the wire regarded as uniform, and the factor 228 was calculated from the dimensions of the wire and the cylinder as given above. The value of \( F \), as thus calculated, which corresponded with an emission current of \( 9.7 \times 10^{-12} \) ampere was called by Millikan and Eyring the "critical" potential gradient. This current of \( 9.7 \times 10^{-12} \) ampere, which I shall call the "critical" current, is, I believe, the smallest one recorded by the authors, and I suppose that it was regarded as the smallest current that could be measured in their experiments with a satisfactory degree of accuracy; in no other sense, apparently, was it "critical." I shall assume for the purposes of this paper that this current could be measured with an accuracy of 1\%. If the accuracy of this measurement was less than I have taken it to be, the accuracy of any numerical conclusions that I may arrive at in the following discussion will be reduced accordingly.

The copper-collecting cylinder was about 6 cm. long, and I shall assume that all the measured field current came from the 6-cm. length of wire contained within the cylinder. But the current came very unequally from different points on the surface of this wire. Millikan and Eyring say, "The 'field-currents' in general have their origin in a few minute surface spots." Microscopic examination of the wire shows, according to Oppenheimer, "that at appropriate positions there are small craters, and that these are surrounded by protuberances with very small radius of curvature; and the dimensions of these points, which should be responsible for the current, vary from a tenth to a fortieth of those of the wire." "Diffraction, however, makes the precise estimation of the radii of curvature of the points impossible." Oppenheimer gives an estimate of the
total area of the effective points as "about $10^{-5}$ that of the wire." I shall presently give a reason, drawn entirely from the data furnished by Millikan and Eyring, for believing it to have been very much smaller than this.

The $F$ of Oppenheimer's equation (3) and of my equation (3') is the potential gradient at these sharp effective points of emission and is therefore very different from, many times greater than, the conventionally calculated $F$ of Millikan and Eyring's expression, $F = 228\phi$.

I shall in what follows use first Oppenheimer's equation (3) and later equation (3').

With Use of Equation (3).—Case 1. The total area of the emission spots is taken to be approximately $10^{-5}$ times the surface area of the 6-cm. length of wire: Taking $F$ "critical" $= 29.3 \times 10^6$ volts per cm., I get from equation (3) $i = 4.61 \times 10^{-21}$ ampere as the contribution per valence electron of the surface atoms subject to the potential gradient $F$.

The number of atoms per cu. cm. of tungsten being about $6.3 \times 10^{21}$, the number of atoms per sq. cm. of the surface will be about $1.58 \times 10^{14}$. The wire being 0.00123 cm. in diameter and, within the receiving cylinder, 6 cm. long, has a surface area of 0.0232 sq. cm., on which are $3.67 \times 10^{13}$ atoms, each with 6 valence electrons, a total of $2.2 \times 10^{14}$ such electrons. If every one of these electrons were subject to the potential gradient $F$, the total field current would be found by multiplying the value of $i$ by $2.2 \times 10^{14}$. The product is $1.02 \times 10^{-8}$ ampere. Now this is about 105,000 times the "critical" field current, $9.7 \times 10^{-12}$ ampere, which the "critical" potential gradient, by definition, would produce. We therefore conclude that only 1 in 105,000 of the surface valence electrons is active in the emission—that is, only this small fraction of the surface atoms are in such a position as to get the full force of the assumed $F$. The active atoms are supposed to be on small protuberances subject to a higher value of the field force than the other surface atoms. The ratio 1 in 105,000 is near enough to the ratio 1 in 100,000 which Oppenheimer appears to accept, and so the value $F$ "critical" $= 29.3 \times 10^6$ volts per cm. may be taken as the one that results from his equation (3) and his estimate of the active emitting area.

Let us now consider how the thermions might be expected to act under this same force $F$. I shall assume that equation (3) can be applied to the thermions by merely reducing the value of $W$. For the valence electrons I have, following Oppenheimer, taken $W$ as 4.7 electron volts. I must now reduce $W$ by subtracting the value of $\lambda'$ as given in table 1. With $T = 300^\circ$K., $W = 4.7 - 0.3 = 4.4$ electron-volts. So for each thermion where $F = 29.3 \times 10^6$ volts per cm. we have by equation (3) $i = 1.16 \times 10^{-13}$ ampere. This is about 25.2 times as great as the $i$ found for a valence electron. If there were 1 thermion for every 2520 valence elec-
trons, or for every 420 atoms, the thermions would furnish 1% of the "critical" current, and if they had done this their effect would perhaps have been perceptible even at 300°C.

But Millikan and Eyring declare that "the 'critical' gradients and the 'field-currents' are completely independent of temperature between 300°C and 1000°C." Let us try at 900°C. With \( T = 900°C, \ W = 4.7 - 0.89 = 3.81 \) electron-volts. Then with \( F \) "critical" still \( = 29.3 \times 10^6, \ i = 4.86 \times 10^{-17} \) ampere. This is about \( 10^4 \) times the value of \( i \) found for a valence electron with the same value of \( F \). Accordingly, if there were 1 thermion for every \( 10^6 \) valence electrons, or for every 167,000 atoms, the thermions would produce 1% of the field current. Apparently they did not make so large a contribution as this.

At 1100°C., according to table 6 of the Millikan and Eyring paper, the effect of the thermions was on the verge of showing at the "critical" potential gradient and did show in some cases, though not in all. Let us, then, try \( T = 1100°C \), still keeping \( F \) "critical" \( = 29.3 \times 10^6 \) volts per cm. We now have \( W = 4.7 - 1.08 = 3.62 \) electron-volts and \( i = 3.04 \times 10^{-18} \) ampere, which is about 66,000 times the value of \( i \) for a valence electron. Accordingly, if there were 1 thermion for every 6,600,000 valence electrons, or for every 1,100,000 atoms, the contribution of the thermions to the field current might begin to show. Comparing the number 1,100,000 with the value of \( (N \div n) \) at 1100°C., as given in table 2, which is \( 5 \times 10^5 \), we see that the two quantities are of the same order of magnitude.

But I am not satisfied with the value of \( F \) "critical" that I have been using. It was so chosen as to make the active emission area equal to about one \( 10^{-5} \) part of the wire surface, microscopic evidence indicating some such ratio. But such evidence was, according to Oppenheimer, dubious, because diffraction "makes the precise estimation of the radii of curvature of the points impossible." A different criterion for the estimation of \( F \) "critical," and apparently a better one, is furnished by the rate of increase of \( i \) when values of \( F \) are increased. Millikan and Eyring, in figure 2 and the accompanying text on p. 55 of their paper, describe a case in which, starting with critical \( F \) and increasing the field to a final value about 2.83 times the initial, they observed an increase of field current in the ratio of 1 to about \( 4 \times 10^7 \).

Now if, going back to the valence electrons with \( W = 4.7 \) electron volts, we increase \( F \) from \( 29.3 \times 10^6 \) to 2.83 \( \times \) this value, 82.9 \( \times \) 10^6, we get from equation (3) \( i = 3.44 \times 10^{-11} \) ampere. But this value of \( i \) is much more than \( 4 \times 10^7 \) times the value given by \( F = 29.3 \times 10^6 \) volts per cm. It is about \( 7.5 \times 10^9 \) times that value of \( i \).

So I shall now start anew with equation (3). **Case 2. "Critical"** \( F \) to be determined by the criterion that increasing \( F \) to 2.83 times \( F \) "critical" shall
multiply the value of \( i \) about \( 4 \times 10^3 \) times: With \( W = 4.7 \) electron-volts and \( F \) "critical" = \( 38.2 \times 10^6 \) volts per cm., I get from equation (3)

\[
i = 1.63 \times 10^{-17} \text{ ampere, and with the same } W \text{ but making } F = 2.83 \times 38.2 \times 10^6 = 108.1 \times 10^6 \text{ volts per cm., I get } i = 6.54 \times 10^{-10} \text{ ampere.}
\]

The second value of \( i \) is \( 4.01 \times 10^7 \) times the first, thus satisfying the ratio-of-increase criterion.

The moderate relative increase of critical \( F \), from \( 29.3 \times 10^6 \) to \( 38.2 \times 10^6 \), that has taken us from the criterion of case 1 to that of case 2, changes greatly the estimated total area of the emission spots. In case 1 this area is about 1 part in \( 10^8 \) of the surface of the wire; in case 2 it is about 1 part in \( 3.7 \times 10^8 \) of the total surface. This makes the number of emitting atoms about \( 10^4 \). I shall presently consider a much smaller estimate of their number.

Let us now discuss the emission possibilities of the thermions under case 2. At \( 1100^\circ \text{K.} \) we have, with \( F \) "critical" = \( 38.2 \times 10^6 \) volts per cm., \( i \) for a thermion = \( 7.80 \times 10^{-14} \) amp., which is 4780 times as great as the corresponding valence electron \( i \). If the number of thermions were to the number of valence electrons as 1 to 478,000, or to the number of atoms as 1 to 79,700, they should furnish 1% of the field current at \( 1100^\circ \text{K.} \) with \( F \) "critical" = \( 38.2 \times 10^6 \) volts per cm. Apparently they did not do so much as this in all cases at \( 1100^\circ \text{K.} \), though in some cases with critical \( F \) their effect was visible at this temperature.

I shall now try equation \( (3') \) instead of equation (3).

**With Use of Equation (3').**—**Case 1, defined as in use of equation (3):**

Taking \( W = 4.7 \) electron-volts and \( F \) "critical" = \( 18.45 \times 10^6 \) volts per cm., I get \( i = 4.61 \times 10^{-21} \) ampere. Multiplying this quantity by \( 2.2 \times 10^{14} \) and dividing by \( 9.7 \times 10^{-12} \), as before, I get 105,000, approximately, as the ratio of the total wire surface to the emitting area. This comes near enough to satisfying the condition of case 1. At \( 1100^\circ \text{K.} \), with \( F \) unchanged, the \( i \) for a thermion would be \( 8.18 \times 10^{-18} \) ampere, and here 1 thermion to about \( 17.8 \times 10^6 \) valence electrons, or to \( 2.96 \times 10^6 \) atoms, would furnish 1% of the field current.

**Case 2, defined as before:** Taking \( W = 4.7 \) electron volts and \( F \) "critical" as \( 26.22 \times 10^6 \) volts per cm., I get \( i = 3.65 \times 10^{-18} \) ampere.* With \( W \) unchanged and \( F \) multiplied by 2.83 I get \( i = 1.44 \times 10^{-8} \). This second \( i \) is \( 3.95 \times 10^7 \) times the first, which satisfies well enough the criterion of case 2.

With \( T = 1100^\circ \text{K.} \), \( F \) remaining unchanged, the value of \( i \) per thermion is \( 1.76 \times 10^{-12} \) ampere. This is 4800 times as great as the corresponding value of \( i \) for a valence electron. Accordingly the thermions, if there were 1 of them for every 480,000 valence electrons, or for every 80,000 atoms, should furnish 1% of the field current at \( 1100^\circ \text{K.} \).

In table 3, I have assembled various estimates of \( n \), the number of
thermions per cu. cm., and of \((N + n)\), the number of atoms to a thermion, in thoriated tungsten. Of the estimates which I have in the preceding pages made from the data of Millikan and Eyring with the help of Oppenheimer’s equation, I shall here retain only those for 1100°K., since in dealing with lower temperatures I have merely found lower limits, perhaps very remote lower limits, for \((N + n)\). I have no assurance that the estimates for 1100°K. are at all close in any one of the several cases considered—there are too many elements of uncertainty for any such assurance. But I think it is fairly evident that we can harmonize the main features of the dual theory of conduction with the experimental data of Millikan and Eyring by supposing the thermions to be very few compared with the number of atoms, not fewer, however, than other evidence would make them.

<table>
<thead>
<tr>
<th>(T)</th>
<th>SOURCE OF DATA</th>
<th>(n)</th>
<th>((N + n))</th>
</tr>
</thead>
<tbody>
<tr>
<td>300°K.</td>
<td>Dushman</td>
<td>1.8 (\times) 10^{15}</td>
<td>35 (\times) 10^{4}</td>
</tr>
<tr>
<td>900°K.</td>
<td>Dushman</td>
<td>5.0 (\times) 10^{15}</td>
<td>13 (\times) 10^{4}</td>
</tr>
<tr>
<td>1100°K.</td>
<td>Dushman</td>
<td>12 (\times) 10^{15}</td>
<td>5 (\times) 10^{4}</td>
</tr>
<tr>
<td>290°K. (?)</td>
<td>Colpitts, film 1</td>
<td>1.4 (\times) 10^{15}</td>
<td>45 (\times) 10^{4}</td>
</tr>
<tr>
<td>290°K.</td>
<td>Colpitts, film 2</td>
<td>(\geq 9) (\times) 10^{15}</td>
<td>&lt; 7 (\times) 10^{4}</td>
</tr>
<tr>
<td>1100°K.</td>
<td>M. &amp; E., with eq. (3), case 1</td>
<td>6 (\times) 10^{14}</td>
<td>1 (\times) 10^{4}</td>
</tr>
<tr>
<td>1100°K.</td>
<td>M. &amp; E., with eq. (3), case 2</td>
<td>8 (\times) 10^{15}</td>
<td>8 (\times) 10^{4}</td>
</tr>
<tr>
<td>1100°K.</td>
<td>M. &amp; E., with eq. (3'), case 1</td>
<td>2 (\times) 10^{14}</td>
<td>3 (\times) 10^{4}</td>
</tr>
<tr>
<td>1100°K.</td>
<td>M. &amp; E., with eq. (3'), case 2</td>
<td>8 (\times) 10^{17}</td>
<td>8 (\times) 10^{4}</td>
</tr>
</tbody>
</table>

*General Conception of Conduction.*—It may at first glance appear as if thermions so few as 1 in 10^5 or 10^6 of the atoms could have only a negligible effect in conduction. It is to be remembered, however, that, if the “free path,” or rather the free time, of a thermion within a metal is terminated only by the capture of the thermion by a metal ion, the conducting power of the thermions is, other things being equal, independent of their number.10

If the thermions are, let us say, 1 to every million atoms, each thermion will be, on the average, about 100 atomic diameters distant from its nearest neighbor thermions. If, as I assume, the positive ions within the metal are equally numerous, or equally few, with the thermions, we naturally ask whether they have any other function in conduction than that of terminating the careers of thermions by capture. Have they anything important to do with the conduction due to the valence electrons, which I have in preceding papers called the “associated” electrons? For many years I have been insisting upon the probability that they do have such a rôle. I am of the same opinion still, but my conception of the manner in which they serve has somewhat changed.

I used to think of “associated-electron” conduction as effected by the passage of individual electrons from atoms to adjacent ions, and I was much concerned with the kinematics of the operation. The conceptions
of wave-mechanics have happily loosened up the relations of valence electrons to their nuclei, and with my growing conviction of the relative fewness of the thermonions, and so of the ions, I have come to think of "associated-electron," or valence-electron, conduction as effected by the intermittent movements of trains of electrons, each train perhaps extending over many atoms. The essential conditions for the movement of a train are a potential gradient and a vacant space—that is, an ion—at the forward end of the train.\(^{11}\)

The conception of electrons as moving in longer or shorter trains through a metal is no novelty, but usually, I think, those who have adopted this conception have made no provision of terminal facilities for such trains. I have made this suggestion before, but I make it now with new emphasis.

Naturally, heat movements of the atoms would tend to break up the trains (Bridgman’s idea) and so, probably, would the presence of atomic inequalities such as would exist in alloys, each influence lessening the conductivity of the metal.

* With this value of \(i\), only 1 in \(8.2 \times 10^6\) valence electrons on the surface of the wire need be active in order to emit the "critical" current, \(9.7 \times 10^{-12}\) ampere. The number of actively emitting surface atoms on the 6-cm. length of wire is thus reduced to about 4400. It appears that in one case (see figure 2, p. 55 of Millikan and Eyring’s paper) the total field-current was about \(4 \times 10^{-4}\) ampere. The question naturally arises whether a current of this strength passing out through a total surface area containing only 4400 atoms would not cause a considerable local heating of the emitting surface.

Assuming as an extreme case that all of the current passes out through a single area, I find by calculation that, if the ordinary laws of electric and thermal conduction hold, with the ordinary values of the conduction coefficients, the emitting surface, if continuous with the general surface of the wire, would be heated only a fraction of a degree above the general temperature of the wire, supposed to be at 300°K. If, on the other hand, this emitting surface were the outer end of a cylinder projecting a distance of 5 times its own diameter straight out from the general wire surface, it might be heated 5 or 6 degrees above the temperature of the wire.

If the total emission current of \(4 \times 10^{-4}\) ampere is supposed divided into ten equal parts, each going out through an emitting surface containing 440 atoms, this surface being the outer end of a cylinder projecting 5 times its own diameter, the surface in question will be heated about one-tenth as much as the larger surface previously considered.

It appears, then, that no considerable local heating of the emitting spots would occur under any of the conditions contemplated in this paper. On the other hand, spots on the receiving copper cylinder opposite the emitting spots on the wire were in some cases heated to luminosity by the electrons projected from the wire.


\(^3\) *J. Franklin Institute*, October, 1928.


A PRELIMINARY REPORT ON THE MEASUREMENT OF THE
Ka LINE OF CARBON

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In a recent paper by Weatherby\textsuperscript{1} the wave-length of the \( K\alpha \) line of carbon is given as 45.4 Å, the weighted mean of a number of individual measurements that agree very well with each other. This value is quite far above that of 44.9 Å as determined by Thibaud\textsuperscript{2} and rather close to that of 45.5 Å, as measured by Dauvillier\textsuperscript{3} using a fatty acid crystal. Thibaud\textsuperscript{2} estimates a maximum possible error in his work of 0.2 to 0.3 Å. On the other hand it is generally recognized that the index of refraction of the crystal used by Dauvillier would give a result that is too high. Consequently it was thought advisable to re-measure the \( K\alpha \) line of carbon. This paper is a preliminary report on this measurement.

The measurements were made by reflection at grazing incidence from a ruled grating in a vacuum spectrograph. The spectrograph used was that described by Osgood,\textsuperscript{4} modified for use with a plane grating. The radiation, after passing through a series of slits to collimate the x-rays and to reduce the intensity of the optical light from the tungsten filament, falls on the grating at a small grazing angle. The size of the ruled surface (3 cm. \( \times \) 3 cm.), the width of the x-ray beam (approx. 0.1 mm.) and the magnitude of the grazing angle (more than 2° 30') make it possible to have the entire beam "reflected" from the ruled surface of the grating. The lower half of the radiation is recorded on a photographic plate placed fairly close to the grating, the upper half on a plate some distance farther back. The direct beam is permitted to fall on the plates by the complete removal of the grating from its path. This arrangement permits all measurements to be made from the centers of the recorded lines. Furthermore, the distance between the two plates together with the separation of the lines on them permits an accurate calculation of the distance from the grating (see the accompanying figure).

\textsuperscript{1} Ibid., 13 (1927), p. 56.
\textsuperscript{5} It seems probable that such a movement would begin at the forward end of the "train" and extend itself backward, somewhat as a railway train starts.