Electron Emission into Dielectric Liquids

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The current between polished nickel electrodes immersed in pure toluene has been measured as a function of electric field (over the range 0 to 250,000 volts/cm) and of temperature (from −15 to 70°C). The Richardson lines are straight but show a very small slope (0.05 to 0.4 ev) and a small value of the constant $A$ ($10^{-8}$ to $10^{-10}$ amp./cm² deg.$^3$). The log $i$ vs. $E^3$ curves show a slope about twice the value $eV/DkT$ predicted by the simple Schottky theory, but in agreement with the theory of Baker and Boltz. It is found however that there are serious objections to this theory, and the agreement with it is probably accidental. The situation is in fact too complex to be handled by a simple theory. It is suggested that for the low potential barrier present at the metal-dielectric interface a combination of thermionic and field currents would be expected which would account qualitatively for the observed behavior.

The conduction of electricity through liquid and solid dielectrics is a phenomenon which is as yet imperfectly understood as the review of the field by Nikuradse$^1$ shows. Even the nature and origin of the conduction currents has been, and still is, in dispute. During recent years the suggestion has been advanced that, in very pure dielectric liquids at least, the currents are caused either by thermionic emission across the metal-dielectric interface or by field emission.

This question has been recently investigated by Baker and Boltz$^2$ who studied the voltage dependence of the current between plane metal surfaces immersed in pure liquid toluene. At high fields they found that the log $i$ vs. $V^3$ curves approximated straight lines whose slopes were greater by a factor $D^1$ ($D=$dielectric constant) than the Schottky lines for thermionic emission in a vacuum. This was in agreement with a theory they proposed for the effect of a dielectric on thermionic emission and they concluded that their results supported the thermionic emission theory.

We believe, however, that serious questions can be raised concerning the validity of their theory of the Schottky effect in a dielectric. In this paper we re-examine briefly the theory of the effects to be expected and present some further measurements on the temperature and field variation of the conduction currents.

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$^1$ A. Nikuradse, Das Flussige Dielektrikum.
$^2$ E. B. Baker and H. A. Boltz, Phys. Rev. 51, 275 (1937). (Additional references to the literature will be found in this paper.)

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**FIG. 1.** Variation of potential energy of an electron near a metal surface in vacuum (upper curve), in dielectric (middle curve), and in dielectric with applied field (lower curve).
(the highest Fermi level) the space charge of electrons escaping out to this point before returning to the surface will prevent the application of the image law. Beyond this point the image law may hold for uniform surfaces. Arbitrarily, then, we set \( W_{a1} = \mu \), the work done against forces within the distance \( x_1 \) (Fig. 1) and \( W_{a2} = W_a - \mu = \phi_0 \) the work done from \( x_1 \) to \( \infty \), \( \phi_0 \) being the usual thermionic work function. If \( f(x) \) is the force on an electron at the distance \( x \) then
\[
W_{a1} = \mu = \int_{x_1}^{\infty} f(x)dx
\]
and
\[
W_{a2} = \phi_0 = \int_{x_1}^{\infty} f(x)dx.
\]
(1)

These equations serve to define \( x_1 \). If, for distances greater than \( x_1 \), \( f(x) \) is the image force, \( e^2/4x^2 \), then \( \phi_0 = e^2/4x_1 \).

When a dielectric is placed in contact with the metal surface the potential barrier will be lowered because (1) the short range forces will be reduced since the outermost layer of positive ions in the metal will have a less asymmetrical position than in the absence of the dielectric atoms and (2) the long range electrostatic forces on an escaping electron (e.g., the image force) will be reduced by a factor \( D \).

Because of the reduction in short range forces the distance at which the potential energy becomes equal to \( \mu \) will be greater, \( x_2 \) in Fig. 1. We will have then in place of (1)
\[
\phi_{DE} = \int_{x_2}^{\infty} f_D(x)dx,
\]
where \( f_D(x) \) is the force on an electron in the dielectric. If the image force predominates we have \( \phi_{DE} = e^2/4DX \). Thus even though the image force is reduced only by a factor \( D \), the work function may be reduced by a much larger factor since \( x_2 > x_1 \). In a qualitative way the picture will be similar if other long range forces in addition to the image force are present.

**Effect of applied field**

Suppose now a uniform electric field, \( E \), be applied at the metal-dielectric surface. The force on an electron in the dielectric near the metal will now be
\[
F = f_D(x) - EE.
\]

Very close to the metal-dielectric interface, however, there will be a layer of polarization charge, located, say, at the average distance \( a \) from the metal. At distances less than \( a \) the field will be \( D\epsilon \) when the field in the dielectric is \( E \). The force on an electron here then will be
\[
F_a = f_D(x) - D\epsilon E.
\]

The total work \( W_E \) required to take an electron from the metal out to the distance \( x_0 \) where the potential energy is a maximum will be
\[
W_E = \int_{0}^{x_1} (f_D(x) - D\epsilon E)dx + \int_{x_1}^{x_2} (f_D(x) - EE)dx
\]
\[
= \int_{0}^{x_1} f_D(x)dx - D\epsilon E[a - E(x_0 - a)] - \int_{x_1}^{x_2} f_D(x)dx
\]
\[
=W'_o - \int_{x_1}^{x_2} f_D(x)dx - E[x_0 + (D - 1)a],
\]
where \( W'_o \) is the potential barrier in the dielectric in the absence of the field. Since \( e\phi_D = W_E - \mu \) and since \( W'_o \) and \( \mu \) do not depend on \( E \) we find
\[
\frac{d\phi_D}{dE} = -\frac{f_D(x_0)}{E} = -\frac{E[x_0 + (D - 1)a]}{dE} = -[x_0 + (D - 1)a],
\]
(2)
since by definition \( f_D(x_0) = E/x \). For \( D = 1 \) (vacuum) this reduces to the usual relation \(^3\)
\[
\frac{d\phi}{dE} = -x_0.
\]

We have assumed \( a \) to be independent of \( E \) which seems reasonable, since the polarization charge will always be as close to the metal as possible. Hence \( a \) will be determined by the molecular structure and should always be of the order of one molecular diameter. At the highest field used in our experiments \( x_0 \) is of the order of 20 molecular diameters, hence \( (D - 1) a \) will be much smaller than \( x_0 \). (For toluene \( D = 2.39 \). In the case of an image field \( x_0 = 1/2\epsilon/ED \) \(^4\) and we then find \( \phi_{DE} - \phi_D = (\epsilon/ED)^{1/2} \). Whence
\[
\frac{d\phi_D}{dE} = -\epsilon/D.
\]

\(^4\) See J. A. Becker, Rev. Mod. Phys. 7, 95 (1935).
depend on $E$) we have then
\[ \frac{d(\log I)}{dE_\perp} = \frac{eI}{D_\perp kT}. \]  (5)

These are the expected Schottky relations for a dielectric and we see that the slope of the log $I$ vs. $E_\perp$ or the $\varphi_0$ vs. $E_\perp$ lines should be $D_\perp$ times smaller than in vacuum.

In the theory of Baker and Boltz the assumption was apparently made that $a = x_0$. If we make this assumption and also assume an image field then Eq. (4) becomes
\[ \frac{d\varphi_0}{dE_\perp} = -(eD_\perp) \]  (6)

and Eq. (5) becomes
\[ \frac{d(\log I)}{dE_\perp} = eI D_\perp / kT, \]  (7)

which are the Baker and Boltz relations.

However, we can see no justification for the assumption $a = x_0$. The point $x_0$ is not a position of equilibrium for positive ions when the field is such as to accelerate electrons. It seems unreasonable to suppose that for weak fields the polarization charge would be located 50 to 100 atomic diameters from the metal-dielectric interface. Hence we set $a < x_0$ and obtain Eqs. (4) and (5).

However it must be emphasized that the failure of experimental curves to follow Eq. (4) may not necessarily imply that the currents are not thermionic but possibly only that the field is not an image field. In this case Eq. (3) would still apply but not Eq. (4).

The situation to be expected in case field emission plays a part will be discussed later.

**Apparatus**

The apparatus used was similar to that employed by Baker and Boltz except that provision was made for measuring the currents as a function of temperature. A diagram of the tube is shown in Fig. 2. The two electrodes were of nickel with carefully polished surfaces. They were first cleaned in boiling NaOH and in dilute HCl and washed in distilled water. They were then heated for several hours at 100°C in an atmosphere of hydrogen to remove oxide layers. The electrodes were mounted in a suitable adjustable support, insulated by fused quartz rods.

Pure toluene ($D = 2.39$) was circulated through the tube by a distillation train not shown. C.P. Toluene was further purified by treatment with H$_2$SO$_4$ and NaOH to remove traces of thiophene. The toluene was then distilled over metallic sodium to remove most of the water while final traces of water were removed by passing the liquid into a reservoir containing two electrodes connected to a high voltage source. After about two hours the top water-free portion was drawn from this reservoir directly into the tube. The evacuated chamber at the lower end of the tube in Fig. 2 was provided to prevent condensation of moisture on the glass near the high voltage lead during the low temperature measurements.

Temperature variation was obtained over the range $-15^\circ$C to $70^\circ$C by filling the copper reservoir around the tube with hot water, ice or dry-ice-alcohol mixtures. Ample time was allowed for thermal equilibrium between readings.

A kenotron rectifier furnished an adjustable voltage up to 30 kv. Control was obtained with an induction regulator in the primary circuit of the transformer. Sufficient filtering for the very low currents used was obtained with a 0.01 µf condenser across the output. A group of 39 200-megohm resistors in series with a galvanometer served as a voltmeter. A 200-megohm protective resistor was placed in the high voltage line to the tube. The currents between the two electrodes
Fig. 3. Richardson plots of currents through dielectric. Figure below each curve gives the value of $E^1$ in (volts/cm)$^4$; figure above each curve gives the slope in e-volts.

were measured either directly with a galvanometer or with a DuBridge-Brown d.c. amplifier.

RESULTS

In order to determine whether the temperature variation of the current across the dielectric obeyed the Richardson equation, current-temperature runs were taken for different applied voltages. When the temperature was first increased above room temperature the current behaved erratically at high voltages, tending to decrease with time after temperature equilibrium was established. However, after reaching a given high temperature, reproducible currents could be measured at any lower temperature. There is presumably some sort of surface layer formed by heating which remains reasonably stable at lower temperatures. This type of irregularity has been found by most investigators in this field and suggests that metal-dielectric interfaces are more difficult to control than vacuum-metal surfaces. This itself suggests that one will expect a more complex behavior than is observed for clean metals in vacuum. In particular, with complex surfaces of the type present here one will hardly expect a simple image law of force on the electrons near the surface.

A series of Richardson plots for applied fields ranging from 400 to $25 \times 10^4$ volts/cm is shown in Fig. 3. The figures below each line give the values of $E^1$. The slope of each curve expressed in electron-volts is indicated by the number above each curve and these vary from 0.41 ev at 0.4 kv/cm to about 0.05 ev for 250 kv/cm. Since the work function of Ni in vacuum is of the order of 5 volts it is evident that even at low applied fields the work function of Ni in toluene is over 10 times smaller than in vacuum. The Richardson slopes then decrease by a factor of 8 as the field is increased to 250 kv/cm.

The three curves $H_1$, $H_2$, and $H_3$ all taken at the same field indicate the variations in position (but not in slope) of curves taken at different times at high fields. At low fields the curves are quite reproducible. The numbering of the points in curve $D$ shows the order in which the readings were taken.

The data of Fig. 3 show that within the rather large errors and over this restricted temperature range, the currents follow the Richardson thermionic equation. While this is in agreement with the hypothesis of thermionic emission it is not of course to be taken as final evidence since other theories also predict an exponential type of current-temperature curve. The most important result of these measurements is the very small slope exhibited by the Richardson curves and the rapid variation of slope with applied field.

If we pick off from the curves of Fig. 3 a series of points corresponding to measurements made at a single temperature but for different applied fields and plot $\log J$ vs. $E^1$ we obtain the curve shown as $A$ in Fig. 4. It is evident that at constant temperature the currents are closely a linear function of $E^1$. This is just the relation to

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4 This result has also been reported by Edler and Zeier, Zeits. f. Physik 84, 356 (1933).
be expected from the Schottky theory of an image field. However, the slope of this curve is about twice as great as that given by the Schottky theory for a dielectric, namely \( e^1/(DkT)^1 \). The slope is actually about \( D^1 \) times greater than for a vacuum instead of \( D^1 \) times smaller.

If, instead of plotting the \( I \) vs. \( E^1 \) curves from the data of Fig. 3, one plots the data obtained in a single run at constant temperature, much less reproducible curves are obtained, one of which is reproduced as curve \( B \) of Fig. 4. Curve \( B \) is very similar to typical curves obtained by Baker and Boltz, agreeing with theirs also in the slope of the upper linear portion. Comparison with Curve \( A \), which was reproduced at several different temperatures, shows the large effect of the "temperature conditioning" process.

The data giving the Richardson slope \( \varphi \) and the thermionic constant \( A \) as a function of \( E^1 \) are shown in Fig. 5. The values were deduced from the curves of Fig. 3, under the assumption that the emitting surface area is the geometrical area of the cathode. It is evident that at low fields both \( \varphi \) and \( A \) vary rapidly with the field but that above \( E^1 = 300 \) \( A \) remains constant and \( \varphi \) falls off linearly with \( E^1 \). Again the slope of the \( \varphi \) vs. \( E^1 \) line is over twice as great as the slope given by Eq. (4), though about equal to the slope predicted by the Baker and Boltz theory, Eq. (6). The assumption that \( A \) is independent of \( E \) made in deducing Eq. (5) is seen to hold for high fields but to fail badly for low fields. It is therefore evident that the linearity of Curve \( A \) of Fig. 4 down to low fields is accidental, resulting from a simultaneous decrease of both \( A \) and \( \varphi \) in such a way as partially to compensate each other.

It will be noted that the values of the thermionic constant \( A \) are only \( 10^{-11} \) to \( 10^{-12} \) of the theoretical value 120 amp./cm\(^2\) deg.\(^2\). Values as small as this might be accounted for by assuming that (1) the emitting area of the cathode is much smaller than the geometrical area, (2) there is a large temperature coefficient of the work function,\(^5\) (3) the surface potential barrier is a complex one having an exceedingly small transmission coefficient, (4) the currents are not (or are only in part) of thermionic origin.

Evidence that the emitting area is indeed smaller than the cathode area is the fact that, after a long series of runs, the anode is covered with small spots of wax-like material, presumably formed by chemical action of the electron stream. The cathode shows no such markings. This phenomena was also reported by Baker and Boltz and attributed to the concentration of the electron current into small pencils emanating from sensitive points or irregularities in the cathode surface. One could hardly assume, however, that the emitting area is only \( 10^{-13} \) of the total since this would require current densities up

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to $10^7$ amp./cm². A factor of $10^4$ in surface area might not be ruled out leaving still a factor in $A$ of $\sim 10^8$ to be accounted for.

There is no way of estimating the importance of the other factors, any one of which might be sufficiently important to account for the observed discrepancy.

**DISCUSSION**

The chief results of these experiments are: (1) The currents between Ni electrodes in toluene obey Richardson’s equation, over the temperature range available, showing a very small slope and small value of $A$; (2) the log $I$ vs. $E^3$ curves are linear with a slope over twice that predicted by the simple Schottky relation for a dielectric.

Neither of these is sufficient either to confirm or to rule out the hypothesis of the thermionic origin of the currents. The agreement of the Schottky slope with the Baker and Boltz equation must be regarded as accidental since the derivation of this equation is open to serious question. The failure to agree with the simple Schottky slope would be accounted for if (a) the field at the surface is not an image field or (b) if the emission came largely from surface irregularities where the actual field is higher than the “geometrical” field. Both of these possibilities find strong support in the experiments themselves so that lack of agreement with Eq. (5) is not surprising.

On the other hand the fact that our results agree approximately with those of Baker and Boltz suggests that something more fundamental is involved than either of the above-mentioned factors. This leads at once to the question of whether the observed currents are really of pure thermionic origin or whether, for example, they may not be attributed to field emission. At first sight it would appear that this could be tested experimentally, for the Fowler-Nordheim equation for field emission is of the form

$$i = Ce^{-a/E}$$

where $C$ and $a$ are constants. However this equation is derived on the assumption that the potential barrier is so high and the temperature so low that the temperature “tail” of the Fermi distribution of electrons may be neglected. When the potential barrier is not large compared to $kT$, however (as in a dielectric), this equation no longer holds. In fact, in this case, the distinction between thermionic and field emission loses its significance.

Referring to Fig. 6 we may say that for a metal-vacuum interface (curve $A$) the thermionic currents consist of the electrons from the extreme tail of the Fermi distribution, the transmission coefficient over the barrier being large but the number of available electrons small. Field currents arise from the penetration of the barrier by the electrons from the main (temperature independent) part of the distribution (transmission coefficient small, number of electrons large). When the barrier is very low (curve $B$), however, there will be, even at fairly low fields, a moderately large transmission coefficient over and through the tip of the barrier and a moderately large number available electrons at the edge of the highest Fermi level. No calculations appear to have been made of the current as a function of field and temperature to be expected in this case. It is easy to see, however, that if penetration of the tip of the barrier is important the currents will vary more rapidly with the field than the Schottky relation would predict since the transmission coefficient depends strongly on the field. Also they will vary less rapidly with the temperature than the Richardson equation would predict, since there is some contribution from the temperature independent part of the Fermi distribution.

This is precisely what is observed experimentally, namely, a large slope for the log $i$ vs. $E^3$ curves and a small slope and small value of $A$ for the Richardson curves. A quantitative test of this hypothesis, however, must await more complete theoretical calculations.

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