values (136 kcal.) obtained by Lozier[27] from data on the products formed by electron impact in CO.

In closing the author wishes to thank Professor Walker Bleakney, under whose direction this work was done, and Professors E. U. Condon and H. D. Smyth for many helpful suggestions. He also would like to express appreciation to Drs. W. Wallace Lozier and Philip T. Smith who, with Professor Bleakney, designed and constructed the apparatus with which this work was done and to Mr. Kiyoshi Morikawa of the chemistry department of Princeton University for supplying samples of very pure methane.

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Thermionic Emission into Dielectric Liquids

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The presence of thermionic emission at ordinary temperatures for cathodes in contact with dielectric liquids is demonstrated. The current voltage relation is shown to obey the law $I=I_0e^{(\epsilon(\epsilon FD)^{\frac{1}{2}}/kT)}$, where I is the current, F the field, and D the dielectric constant of the liquid. This is a modification of the Schottky law in vacuum. The effects of adsorbed hydrogen and oxygen, of surface irregularities, and of work function are discussed. The formation of a wax by electron bombardment of the liquid is also reported.

A. Introduction

Many theories have been advanced to explain the mechanism of current conduction in pure dielectric liquids in the region of high field strengths. A good resume of these may be found in Nikuradse's book.[1] The most generally accepted of these is the process of ionization by collision, in analogy to gaseous conduction. It is assumed that ions are initially present in the liquid which are the current carriers at low field strengths. These are supposed to be formed by some ionizing agent such as x-rays or cosmic rays, or from ordinary electrolytic dissociation. At intermediate field strengths this ion current saturates and becomes independent of field until such a value is reached that the ions (or electrons) attain sufficient velocity to form new ions by collision. New ions are formed at such a rate that the current becomes an exponential function of the voltage $I=I_0e^{cV}$ which is found to agree fairly well with experiment, considering I_0 and C as adjustable constants. Most published data available to the authors are not sufficiently accurate, however, to distinguish this relation from $I=I_0e^{c\sqrt{V}}$, for example.

In contrast to the above view, the results obtained in our investigation prove that, in the case of the liquid investigated (pure toluene), at least, the only important means of current conduction is by electrons emitted from the cathode thermionically.

This mechanism was first proposed in tangible form by H. Edler and O. Zeier[2] who found the temperature variation of the current to correspond to the Richardson equation for thermionic emission. Although they did not derive the current voltage relation given in this paper they found the current to vary less rapidly with voltage than $I=I_0e^{cV}$.

L. Inge and A. Walther[3] also disagree with the mechanism of ionization by collision and invoke instead the cold cathode effect, which would require a current voltage relation of the form $I=I_0V^2e^{-c/V}$. They plot essentially log I/V^2 against $1/V$ and obtain not a straight line, but a curve which they believe to be approaching a straight line in its high voltage portion. However, if their data are replotted as log I against $\sqrt{V}$, a straight line is obtained in verification of the formula $I=I_0e^{c\sqrt{V}}$ of the present paper.

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[1] A. Nikuradse, *Das flüssige Dielectrikum*, pp. 135–136.

[2] H. Edler and O. Zeier, Zeits. f. Physik **84**, 356 (1933).

[3] L. Inge and A. Walther, Tech. Phys. U. S. S. R. **1**, 539 (1935).

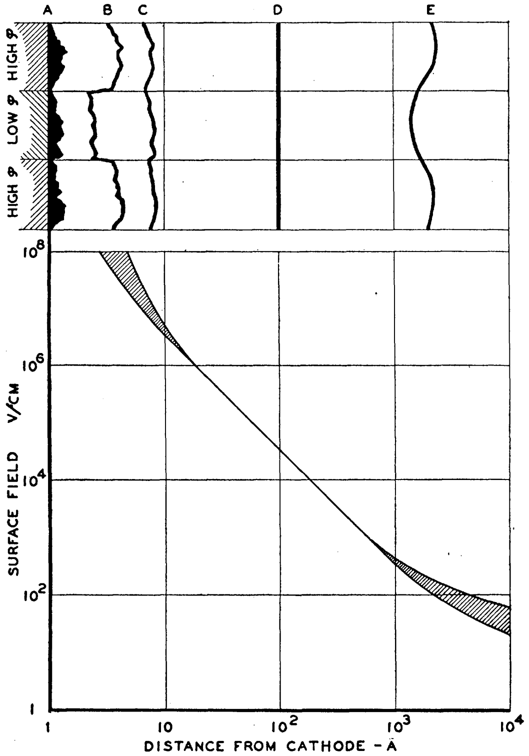

FIG. 1. Intrinsic surface fields.

B. THEORY

I. In vacuum

The emission of electrons from a hot cathode in a vacuum is governed by the well-known Richardson law, $I = AT^2 e^{-\epsilon\varphi/kT}$ where I is the current density, φ is the work function in electron volts and $\epsilon\varphi = \chi$ is the amount of energy required to remove an electron from the metal to a vacuum. If a sufficient extracting field is applied to the cathode the current becomes saturated except for the Schottky correction, which introduces a dependence upon the field F of the form

$$I = AT^2 e^{-\epsilon\varphi/kT} e^{\epsilon(\epsilon F)^{\frac{1}{2}}/kT} = I_0 e^{\epsilon(\epsilon F)^{\frac{1}{2}}/kT}.$$

This Schottky relation, suitably altered to include the effect of a medium possessing a dielectric constant greater than unity, provides the limiting form at high fields of the current-voltage relation for electronic conduction in a dielectric liquid. Before introducing this modification, it will be convenient to make a few remarks about the Schottky law in vacuum which will also be pertinent when the dielectric liquid is present.

Becker and Mueller[4] have shown that the electrons emitted from the cathode surface must have a normal component of velocity sufficient to project them beyond the attracting influence of the surface fields, into the region where these fields are smaller than the external extracting field. They have shown that these fields may be divided into three classes according to their range of action. First, are the powerful but extremely short range fields of the metal atoms that are responsible for the major portion of the work function. Second, are the image forces which predominate out to about 10^{-5} cm. At still greater distances, forces due to nonuniformities of the work function over the surface are most important.

At the actual surface of the metal the atomic fields are of the order of 10^8 volts/cm which is the magnitude required for the cold cathode effect. Moving out from the cathode, the intrinsic field falls off rapidly and it is possible to neutralize it, or to produce a surface of zero field strength, by applying an external field. The distance of this surface of zero field from the cathode is dependent upon the strength of the applied field. On the cathode side of this surface, the net field is in the sense that tends to return electrons to the cathode, and on the other to send them to the anode. An electron consequently must have sufficient initial velocity to reach this surface against the adverse field in order to be emitted.

In Fig. 1, the surface fields are plotted against distance on a logarithmic scale. In the range in which the image field predominates, the curve becomes a straight line corresponding to the function $F_i = \epsilon/4z^2$, where z is the distance of the electron from the cathode, and ϵ is its charge. Above several hundred angstroms the patch fields are most important and below about 10A the atomic fields of the metal atoms assume control. Each end of the curve is shown to broaden out, representing the possible variations in value of the field at various points over a plane surface parallel to the plane cathode, due to patchy work function, and in the case of the short range fields, to surface irregularities as well.

A cross section showing the zero field surfaces

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[4] J. A. Becker and D. W. Mueller, Phys. Rev. **31**, 431 (1928).

for various applied fields is pictured above the graph. If the metal surface, A, is not perfectly plane and of uniform work function, only those zero field surfaces, such as D lying within the effective range of the image force will be plane.

The geometrical surface irregularities that exist even on a highly polished electrode cause deviations from the Schottky law at high applied fields. Points cause most of the emission from a surface of uniform work function, if the applied field is high enough to cause the surface of zero field (C) to be appreciably distorted by their presence. Thus, the more nearly flat the cathode is, the higher must be the applied field, or the closer to it must be the surface of zero field, in order to have the effect of points of any consequence. In investigating the cold cathode effect, it must be flat even on an atomic scale in order to avoid the influence of points.

If the applied field is F, and the surface is perfectly plane, we have the ordinary Schottky relation. If, however, a point exists on the surface, the applied field at the tip of the point is not F but p_0F, where p_0 is a field factor (>1) depending on the sharpness of the point. At the surface of zero net field, the applied field is pF, where p is a function of F, equal to p_0 at the point and becoming unity at a sufficient distance from the cathode. The Schottky relation for the current from the point is

$$I = I_0 e^{\epsilon(\epsilon p F)^{\frac{1}{2}}/kT}.$$

If the point is sufficiently sharp, i.e., if p is large, the contribution of current from the point may overshadow that for all the remainder of the surface. This modified relation may be approximately obeyed if a number of points of about the same size exist simultaneously.

Since p is a function of F, a straight line will not be obtained if $\log I$ is plotted against $\sqrt{F}$ as is commonly done to illustrate the Schottky effect. Instead, a curved line having increasingly greater slope with increasing field will result. However, if p is a slowly varying function of F, the curvature is slight and the curve may appear straight over the portion investigated, but will be too steep. Since the knee of the curve $\log I$ *vs.* $\sqrt{F}$ obtained experimentally (caused by the approach to the limiting Schottky line) has the opposite curvature, a point of inflection is produced and the appearance of straightness enhanced.

The Schottky law is derived on the assumption that the image law force $F_i = \epsilon/4z^2$ is the only long range force of importance. This is accomplished[5] by showing that an external field, F, produces a change $\Delta\varphi = (\epsilon F)^{\frac{1}{2}}$ in the effective work function by neutralization of the image force at the critical distance $z_c = (\epsilon/4F)^{\frac{1}{2}}$ from the cathode surface. At lower applied fields the effect of the patch fields overshadows the image law and the Schottky law does not apply.

II. Modification introduced by the presence of a dielectric liquid

If we replace the vacuum by a dielectric liquid we may expect the phenomenon to be altered by the following considerations:

1. *The work function will be lowered* because the amount of energy necessary to transfer an electron from the metal to a vacuum is greater than that required to transfer it to a dielectric liquid. This difference in energy corresponds to the energy necessary to remove a "free" electron from the liquid to a vacuum. By a free electron in a dielectric liquid we mean an electron not in "chemical" combination with molecules of the liquid but simply immersed in it, the polarizing forces its field exerts on the surrounding molecules of the liquid being responsible for the difference of energy in question, which we may term the "heat of immersion of an electron." We may expect that this amount of energy will be independent of the nature of the metal, and as a result that the relative order of the metals in the photoelectric series will be the same as in vacuum. We may also predict that the amount of the lowering of the work function will be at least roughly dependent upon the dielectric constant of the liquid, being greatest for liquids of highest dielectric constant.

2. *The temperature used must be lower* since the dielectric liquid would boil or decompose at the temperatures used in studies of thermionic emission in vacuum. Since T and φ occur in reciprocal relation in the exponent of Richardson's formula, we may expect that a lowering of both T and φ simultaneously will permit appreciable emission

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[5] J. Becker, Rev. Mod. Phys. **7**, 108 (1935).

at room temperature, if φ is lowered to such an extent that the ratio is not greatly altered.

3. *The saturation of the current will be much less complete* at high fields partly because the temperature is lower; the exponent in the Schottky correction is consequently larger, and the dependence on the field of more importance. In addition, the Schottky correction must be modified by the fact that the image force is weakened by the presence of a liquid of dielectric constant greater than one. The image force in a dielectric of dielectric constant D is $F_i=\epsilon/4z^2D$, the distance from the cathode of the surface of zero field is $z_c=(\epsilon/4FD)^{\frac{1}{2}}$, and the revised Schottky correction is

$$I=I_0e^{\epsilon(\epsilon FD)^{\frac{1}{2}}/kT} \quad \text{or} \quad \log_{10}\frac{I}{I_0}=\frac{1.91(FD)^{\frac{1}{2}}}{T}$$

with F in volts per cm.[6] This is the form that the current voltage characteristic takes at high fields. The slope of the line $\log_{10} I=c\sqrt{F}+\log I_0$ is much greater than in a vacuum.

As a rule, somewhat higher fields are required to obtain the straight line portion of the curve than is the case in vacuum. For a given field strength, the surface of zero field as determined by $Z_c=(\epsilon/4FD)^{\frac{1}{2}}$ lies closer to the cathode, and the effect of points on the surface is much more pronounced. Stated in other words, in order to avoid the effect of points, a much smoother surface must be employed as cathode in a dielectric liquid, than is necessary in vacuum.

4. *Collisions of electrons with, and attachment to molecules of the liquid may interfere* with the direct application of the theory of emission in vacuum to that in a liquid. Evidently, however, these are of minor importance for toluene since the data agree with the modified Schottky equation. At low fields collisions and attachment to molecules may be of importance but it would be difficult to distinguish their effects from effects caused by patchy fields.

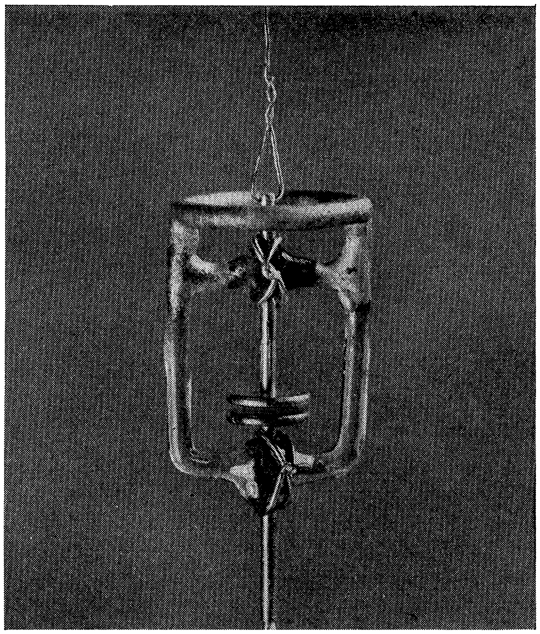

FIG. 2. The electrodes and quartz support.

The authors have observed evidences of chemical action caused by electron bombardment. If high field strengths are used and electrode conditions are such that high currents are flowing, enough of a wax-like substance is deposited on the anode to be readily discernible in about a week's time. This substance is similar in appearance, and in its complete insolubility in organic liquids, to the substance called X which is often observed in underground power cables having oil and paper as a dielectric. Its presence there has always been ascribed to electron bombardment, resulting from discharges in gas pockets in the insulation. This work, however, shows that it may also be produced in the liquid phase alone by electrons produced thermionically, and therefore that its presence does not presuppose the existence of gas pockets, or voids.

It is conceivable that the molecules of some liquids might have sufficient electron affinity seriously to impair or completely to suppress the electron emission altogether by attaching the electrons before they reach the surface of zero field. In such an event the ions thus formed would be discharged again at the cathode.

C. Apparatus

The electrodes used were platinum-iridium and nickel, turned to the form shown in Fig. 2. The faces were ground flat and polished on a metallographic wheel. The electrodes were then tied with wire of the same metal to the small quartz

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[6] One may obtain this expression by introducing the new value of the image force in Becker's derivation of the Schottky correction (reference 5).

frame shown, being aligned by means of grooves ground in the quartz. The bottom electrode shank was drilled so that the assembly could rest on a tungsten point serving as a high voltage lead in. The upper electrode was drilled perpendicular to its axis near the end to receive a stiff platinum wire serving as a measuring lead and as a means of carrying the assembly.

The quartz ring shown was platinized. It made contact with a platinized ring in the apparatus proper, and served as a leakage guard. A guard to preserve a uniform field is neither necessary nor desirable.

The electrode distance was determined by means of a traveling microscope after the assembly was in place.

The apparatus proper is shown in Fig. 3. It consists of a boiler containing toluene and metallic sodium, a central mixing chamber and the electrode chamber. It was designed to permit ready accessibility to the electrodes and the addition of soluble impurities to the toluene without allowing the entrance of air or moisture. By continued distillation from sodium the toluene is constantly repurified and desiccated, and the electrode chamber is continually washed out with fresh toluene.

Since the present work is concerned only with the demonstration of the presence of thermionic emission and the agreement with the modified Schottky law, the absolute value of the work function itself is of importance only insofar as it effects the general order of magnitude of the currents obtained. Consequently, it is not necessary to work in high vacuum, which would be extremely difficult in the presence of an organic liquid. A nitrogen atmosphere was maintained, however, partly to avoid oxidation of the toluene during distillation, and partly because adsorbed nitrogen is known[7] to have a comparatively small effect on the work function of a cathode in vacuum. The effect of other adsorbed gases will be treated in connection with the experimental results.

The toluene vapor leaving the boiler passed over metallic sodium held in a bend in the tube leading from the boiler to further aid in removing moisture, part of which may distill before it can react with the sodium immersed in the toluene. The vapor condensed in the two water condensers, which served to protect from the vapor the ground glass joints, by means of which the electrodes and foreign substances were introduced.

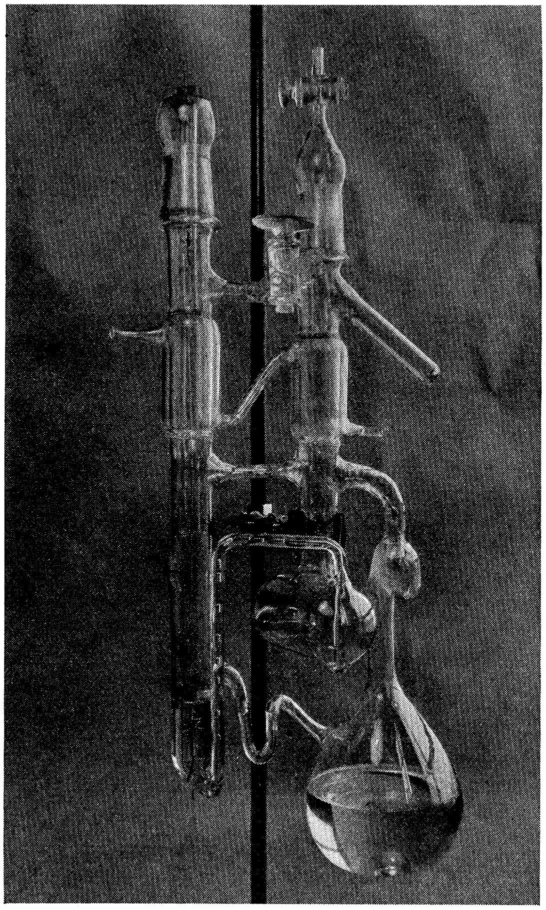

FIG. 3. The electrode chamber and still.

A stopcock attached to a cross arm connecting the two entrance tubes led to a P_2O_5 drying tube, a pyrogallol bulb and a rubber bag reservoir. A stream of nitrogen flowed through this train whenever a joint was opened, preventing the influx of air and moisture.

A siphon connected the mixing reservoir with the electrode chamber permitting either a continuous flow of toluene from one to the other or an accumulation of toluene in the mixing chamber, which may later be run through the electrode chamber. This is accomplished by tilting the apparatus, which introduces a few gas bubbles

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[7] J. H. de Boer, *Electron Emission and Adsorption Phenomena* (Cambridge Press, 1935), p. 147.

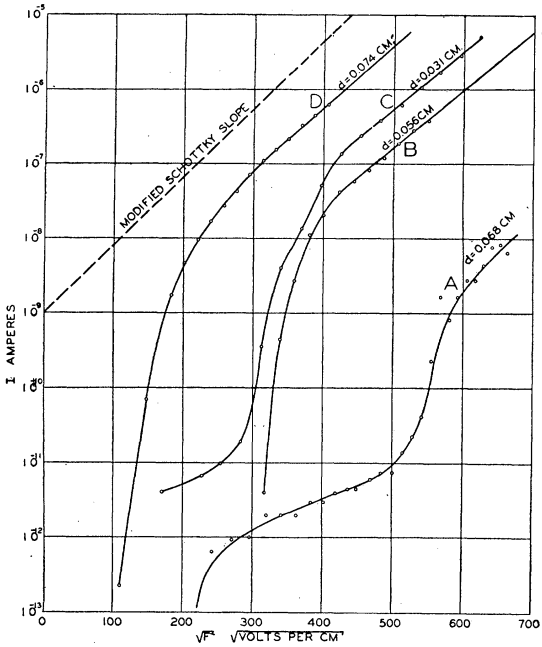

FIG. 4. Current-voltage characteristics for *A* oxygen on platinum-iridium, and *B*, *C*, *D* hydrogen on platinum-iridium. Temperature was 45°C.

in the siphon, stopping its action until the level in the mixing chamber is high enough to start the siphon again. Foreign materials may be added to the accumulated toluene, which is then siphoned to the electrode chamber.

In some cases the electrodes were heated in vacuum by means of radiofrequency induction, cooled and then quickly transferred to the apparatus, exposing them to the air only for a short time. In this way the nature and amount of adsorbed gases could be controlled sufficiently well for the present purpose.

The electrical equipment has been described previously.[8]

The toluene used was C.P. grade further treated with mercury, concentrated sulphuric acid, sodium hydroxide, washed with water, and distilled from metallic sodium before introduction into the apparatus.

D. EXPERIMENTAL RESULTS

The electrodes first used were made of platinum-iridium, because they were easy to clean by washing with chromic acid, then with distilled water and finally heating in a gas flame. Extremely low conductivity was observed even at high field strengths the first few times they were treated in this manner. Thereafter the conductivity became progressively higher with each treatment although there was no reason to suspect any change in the composition of the toluene. It was suspected that the electrodes had absorbed hydrogen from the flame, and heating them in a vacuum confirmed this.

Evidently an adsorbed layer of hydrogen lowers the work function in the same manner as in vacuum.[9] Now it is well known that it is extremely difficult completely to outgas platinum by heating in vacuum, but that it is easily possible to replace an adsorbed layer of hydrogen by one of oxygen, by heating platinum in oxygen, and conversely oxygen may be displaced by heating in hydrogen. Nitrogen, however, has little tendency to be adsorbed, or if adsorbed, does not appreciably affect the work function of platinum.

These facts offer a method of control of the condition of the surface, even if the electrodes be transported through air after the desired condition is attained. It was found possible to produce low or high conductivity at will by having a layer of oxygen or of hydrogen on the surface. Fig. 4 shows current-voltage characteristics for platinum-iridium electrodes plotted as log *I* *vs.* $\sqrt{F}$. Curve *A* is for adsorbed oxygen and curves *B*, *C* and *D* for adsorbed hydrogen. Comparing curves *A* and *D*, we observe a ratio of the currents of the order of 10^5, an enormous difference, which incidentally proves that all but an entirely negligible portion of the current represented by curve *D* is due to electrode condition, since the purity of the toluene was the same for *A* and *D*. This eliminates the possibility of the current being due to ions generated in the liquid by ordinary electrolytic dissociation, even at fields as low as 10 kv/cm.

Adsorbed layers of hydrogen and oxygen on platinum are present,[10] at least for the most part, in ionic form. In the case of hydrogen the ions are positive. This positively charged layer lowers the effective work function by tending to attract electrons out of the metal surface. Together with

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[8] E. B. Baker and H. A. Boltz, Rev. Sci. Inst. **7**, 50 (1936).

[9] Cf. de Boer, reference 7, pp. 149–151.

[10] de Boer, reference 7, p. 150.

their image charges in the metal these ions form dipoles which on the cathode are oriented in the same direction as the applied field. In addition they are to a certain extent mobile on the surface,[11] even at room temperature. On a perfectly flat cathode, i.e., where the applied field is strictly constant, there will be no tendency for these dipoles to be displaced by the field. If, however, hills and valleys exist, they will be driven to the valleys, toward the regions of lowest field. The oxygen dipoles, since their orientation cannot be greatly influenced by the applied field, will be driven to the points. When the applied field is removed, they will again distribute themselves more uniformly over the surface by virtue of their mutal repulsion and by thermal diffusion.

Since an adsorbed layer of hydrogen lowers the work function, and since the hydrogen ions are driven to the valleys on the cathode, where the applied field is *less* than that calculated from the applied voltage and the distance with the assumption that the cathode is plane, we may expect that the slope of the Schottky line will be *less* than for a plane surface, i.e., $p<1$. That this is indeed the case may be observed in curves *B*, *C* and *D* of Fig. 4.

In the case of adsorbed oxygen the ions are driven to the points, but since oxygen increases the work function, the points are thereby rendered relatively inactive and the remainder of the surface being partially cleared of oxygen by the field, contributes most of the current, by virtue of its lower work function. This fact enables us to obtain a closer agreement with the theoretical slope, since the remainder of the surface, devoid of the points, is practically flat. This could not be done in the case of platinum because the approach to the Schottky line lies at such high field strengths (curve *A*) that breakdown is too imminent. In fact, while the current from oxygen on platinum is very low, it is erratic due to the sporadic removal of oxygen by the applied field, which suddenly exposes points of relatively low work function. Thus while an adsorbed layer of oxygen serves as a protection from large electron currents, its removal by the field may perhaps be a cause of breakdown for electrodes in this condition, and electrodes usually *are* in this condition unless specially treated.

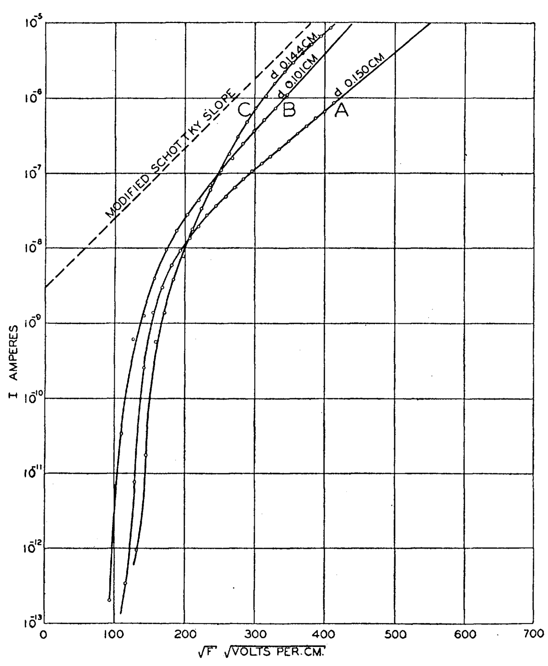

Fig. 5. Current-voltage characteristics for *A* and *C* hydrogen on nickel and *B* nickel. Temperature was 45°C.

It may be emphasized at this juncture that the effective emitting area of the cathode was not entirely under control in these experiments. A displacement of a Schottky line parallel to itself can occur either as a result of a change in emitting area or a change of work function. The slope of the line, however, is independent of these factors, and depends only on the dielectric constant, the temperature and absolute constants (except if $p \neq 1$). Thus, while the fact that the curves exhibit a straight line portion plotted in this manner is in itself good proof of the theory, the additional fact that the slope of this line has exactly the correct value, independent of the distance *d* between the electrodes, cannot possibly be attributed to chance agreement. Other attributes of the current, such as its instantaneous response to voltage changes (except with large amounts of adsorbed gases, which diffuse somewhat slowly at room temperature) are also in accord with the theory.

The work function of platinum is about 6 volts, that of nickel about 5 volts. We may therefore expect greater emission from nickel

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[11] de Boer, reference 7; also E. K. Rideal, *An Introduction to Surface Chemistry* (Cambridge Press, 1930).

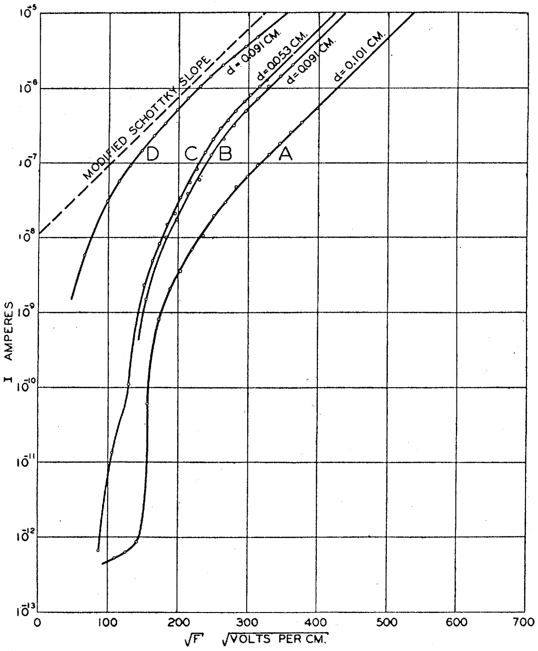

FIG. 6. Current-voltage characteristics for oxygen on nickel. Temperature was 45°C.

than from platinum. In addition, we may expect the work function of nickel to be less influenced by adsorbed hydrogen than that of platinum, as is the case in vacuum, since the adsorbed ions are less firmly bound on nickel than on platinum because of its lower work function.[12]

In Fig. 5, curve *A* was obtained with a nickel electrode that had been heated in hydrogen. It shows the smaller slope characteristic of emission from valleys. Curve *C* was obtained by partially outgassing the electrodes and still shows the effect of hydrogen. Curve *B* was obtained by extreme outgassing over a period of 20 hours. Even though transferred to the apparatus through the air the nickel was partially bare and the curve exhibits the steeper slope due to the presence of points not covered by oxygen.

In Fig. 6 curves *A*, *B* and *C* are examples of nickel outgassed to remove hydrogen, and then soaked in oxygen at room temperature. They all show the correct Schottky slope.

Curve *D* in Fig. 6 was obtained by adding iodine to the toluene. In this case the effect of adding iodine may be seen by direct comparison with curve *B*, which represents the condition just previous to the addition. Since iodine is an electronegative element, it should behave in a manner analogous to oxygen and therefore raise the work function, and decrease the current. Instead, the current was increased considerably. This increase may possibly be attributed to the electrolytic deposition of hydrogen on the cathode supplied by the hydroiodic acid liberated by the action of iodine on toluene, which takes place very slowly at ordinary temperatures. The fact that the slope of the high field portion of the curve is less than the theoretical supports this view. The current represented by curve *D*, once established, was independent of the iodine concentration, being unchanged by repeated washing out of the electrode chamber with fresh toluene. It had all of the properties of an electron current. This curve was included particularly to illustrate the large electron currents that are possible even at low fields.

Since we have shown that these electron currents not only impair the insulating qualities of dielectric liquids but can cause chemical deterioration of them as well, the possibility of increasing the work function of electrodes such as the conductor in oil insulated cable, becomes evident. It is curious, in this connection, that the presence of oxygen should appear to be beneficial, since it has long been considered to be harmful because of the danger of oxidation of the organic insulating liquid.

In conclusion the authors wish to express their appreciation of the efforts of the personnel of the research laboratory whose cooperation made this work possible.

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[12] de Boer, reference 7, p. 151; R. W. Gurney, Phys. Rev. **47**, 479 (1935).

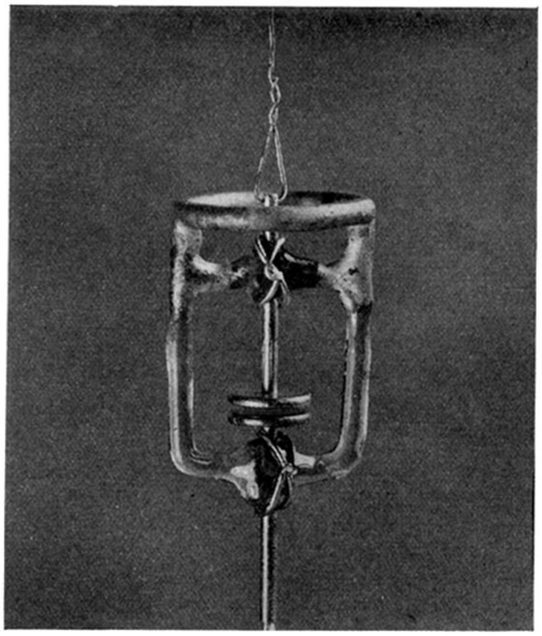

FIG. 2. The electrodes and quartz support.

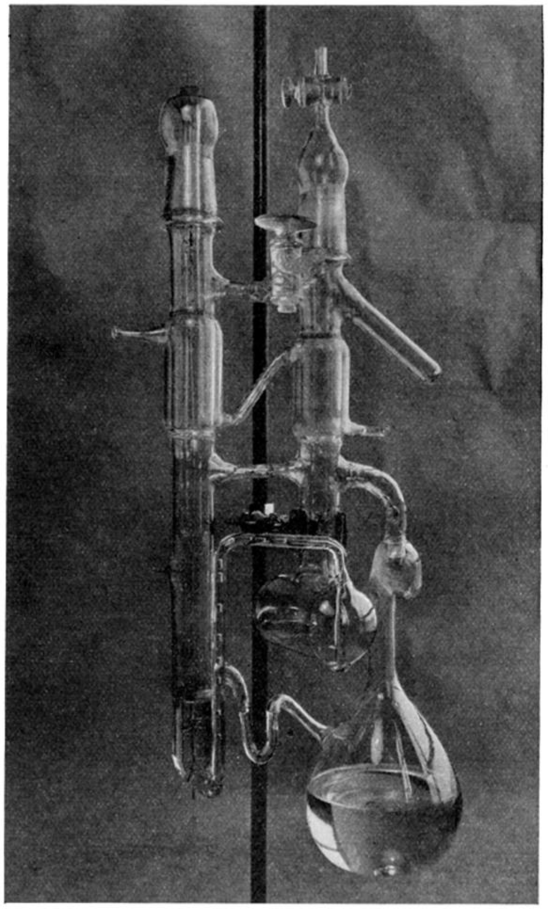

FIG. 3. The electrode chamber and still.