

LETTERS TO THE EDITOR

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Communications should not in general exceed 600 words in length.

Thermionic Emission into Dielectric Liquids

In a recent letter to the editor of *Physical Review* K. H. Reiss<sup>1</sup> has stated his belief that the "potential dissociation effect," rather than thermionic emission is the proper explanation of the authors' data,<sup>2</sup> as well as previous data obtained by Nikuradse,<sup>3</sup> which were used by Reiss<sup>4</sup> in support of the potential dissociation theory of conduction in pure liquids.

The two theories give identical current field strength relations with the exception of the manner in which the dielectric constant  $D$  appears. Thus:

- (1) Reiss  $I = I_0 \exp [\epsilon^{1/2} F^3 / KTD^3]$ .
- (2) Baker and Boltz  $I = I_0 \exp [\epsilon^{1/2} F^3 D^3 / KT]$ .

The slope of the straight line  $\log_{10} I$  vs.  $F^3$  is less than the Schottky slope for a vacuum  $\epsilon^{1/2} / 2.3KT$  for formula (1) and greater for formula (2).

We wish to point out that the "theoretical" slopes in Reiss' paper<sup>4</sup> were *incorrectly calculated* and that the agreement with experiment which he obtained is *entirely spurious*. This may be seen from Table I. It will be observed that in each case the experimental slopes are greater than the Schottky slope for a vacuum and thus cannot possibly be explained by formula (1). In the case of the practically nonpolar liquids, hexane and toluene, the experimental slope is greater even than that given by our formula (2), which we interpret to mean the existence of sharp points on the cathode surfaces. In the case of polar chlorbenzene the lower value is to be interpreted as resulting from the smaller effective dielectric constant caused by dielectric saturation at high field strengths.

These data of Nikuradse were selected from others having lower slopes, according to Reiss.<sup>4</sup> We submit that no data for which this variation of slope is not understood nor under control can be safely used to check either formula.

TABLE I. Slopes of the line  $\log_{10} I/I_0 = K\sqrt{F}$  with  $F$  in volts/cm and  $T = 300^\circ K$ . Here  $K_{vac} = \epsilon^{1/2} / 2.3KT = 1.91/T = 0.00637$ .

Liquid	Hexane	Toluene	Chlorbenzene
Dielectric constant $D$			
I. C. T.	1.874	2.39	5.44
$K_R = K_{vac} \cdot 1/D^3$	0.00465	0.00412	0.00273
$K_{BB} = K_{vac} \cdot D^3$	0.00872	0.00985	0.01486
Experimental slope of Nikuradse obtained from Fig. 2 of Reiss' paper, reference 4.	0.0177	0.0146	0.0078

Therefore even the qualitative variation of slope with  $D$  may not be determined from data selected *arbitrarily*. The authors, however, had a controllable and naturally explained basis of selection, and obtained exact quantitative agreement with formula (2) for toluene.

We realize the desirability of obtaining data for other pure liquids than toluene and intend to do this in future work. The case does not rest on this point, however, since the potential dissociation theory is unable to explain many other facts, such as the very great dependence of the current (and also the slope of  $\log I$  vs.  $F^3$ ) on the material and roughness of the cathode surface. As we have shown,<sup>2</sup> these may be varied in a known and reproducible manner to produce the results expected from the thermionic emission theory.

The potential dissociation theory has the unattractive feature of requiring the presence of ionizing impurities. We do not believe that sufficient impurities are present in a carefully purified liquid, at least one of low dielectric constant such as toluene, to produce this effect.

Reiss has also presented the argument that since theoretically one would expect a lowering of the work function in the presence of a dielectric liquid, and since his measurements<sup>5</sup> of the photoelectric cut-off with and without liquid are almost identical (and therefore, he concludes, there is no lowering of the work function), there can be no thermionic emission at room temperature into a liquid.

The authors believe that all of the photoelectric current in the presence of a liquid will not be collected, particularly near cut-off, since the free path of an electron in the liquid is only one or two hundred angstroms. Electrons released by light of wave-length near the cut-off will not have sufficient kinetic energy to escape the surface fields *in spite of collisions*, unless the extracting field is sufficiently great to neutralize the surface fields at a distance from the surface approximating the free path. If such an extracting field is applied, however, thermally emitted electrons will also be collected. We therefore believe that it is not possible to measure the true photoelectric work function in the presence of a liquid; a value greater than the true value will be found.

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<sup>1</sup> K. H. Reiss, *Phys. Rev.* 51, 781 (1937).

<sup>2</sup> E. B. Baker and H. A. Boltz, *Phys. Rev.* 51, 275 (1937).

<sup>3</sup> A. Nikuradse, *Ann. d. Physik* 13, 851 (1932).

<sup>4</sup> K. H. Reiss, *Zeits. f. physik. Chemie* 178, 37 (1936).

<sup>5</sup> K. H. Reiss, *Ann. d. Physik* 28, 325 (1937).