One of the most interesting aspects of the mutual agreement of the logarithmic curves consists in the inference that the horizontal displacements necessary to bring the curves to coincidence are identical with the differences $(h/e)\Delta\nu$. On this basis, it appears possible to determine h/e from empirical energy distribution curves which are not in agreement with the Fowler-DuBridge theory. This procedure would, of course, be considerably strengthened by an adequate theoretical explanation of the shape of these curves. Meanwhile it may be of interest to note that an evaluation of the present data from this point of view gave h/e values within one percent of Birge's[14] weighted mean. A further increase in accuracy would thus open the possibility of using empirical curves of this type for a precise photoelectric redetermination of h/e.

ACKNOWLEDGMENTS

The author takes pleasure in acknowledging his indebtedness to Professor W. V. Houston, who suggested this investigation, and has always taken an active interest in its progress, and to all staff members of the Norman Bridge Laboratory who have generously contributed their advice on many technical problems.

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[14] R. T. Birge, Nature **137**, 187 (1936).

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The Surface Photoelectric Effect

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The probability of ejection of an electron in the surface photo-effect is expressed in terms of a function of the potential barrier, the energy of the electron after ejection, and the frequency. This function is dominated, for low energies of ejection, by the transmission coefficient of the surface. It is then assumed that the function can be expanded in a power series in terms of the energy of the electron after ejection. In calculating the total emitted current it is shown that the power series development leads to a series of distinctive functions expressing the current in terms of the frequency and the stopping potential. Each of these functions has its own temperature dependence, so that from a complete knowledge of the energy distribution and the temperature dependence of the emitted current it would be possible to draw conclusions as to the nature of the potential barriers. By comparing the theoretical expressions with the observed curves of Overhage, and of Mann and DuBridge, it is possible to conclude that the transmission coefficient of Overhage's anode and of the sodium cathode used by Mann and DuBridge vanished linearly with the diminishing energy of the ejected electrons.

SINCE the development of the quantum theory of solids various attempts have been made to give a theoretical account of the photoelectric emission from metals. The general problem can be divided into two parts which have frequently been treated separately. The first part concerns the interaction of the light with the electrons in the metal and the computation of the probability of ejection. The second part concerns the effect of the statistical distribution of the electrons in the metal on the distribution in energy of those ejected, and the effect of the temperature on the photo-current.

Perhaps the outstanding conclusion from the study of the first problem was the recognition by Tamm and Schubin[1] of the distinction between the surface effect and the volume effect. They pointed out that it is the interaction of the free, or conduction electrons, with the surface potential barrier which makes possible the simultaneous conservation of energy and momentum in the interaction. This cleared up a difficulty of long standing which had been emphasized by

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[1] I. Tamm and S. Schubin, Zeits. f. Physik **68**, 97 (1931). Also H. Frohlich, Ann. d. Physik **7**, 103 (1930).

Millikan.[2] The experimental evidence shows quite clearly that the photoelectrons have been free within the metal and have been bound by the surface work function only, and yet the theory also shows that truly free electrons can not absorb the radiation. The recognition that the surface potential barrier provides sufficient binding to satisfy the theoretical requirements, cleared up the difficulty. In the volume effect, on the other hand, the conservation of energy and momentum is made possible by the binding of the electrons to the atoms in the crystal lattice. Tamm and Schubin gave reasons for believing that the selection rules imposed by the periodic structure of the lattice, prevent the onset of the volume effect until a frequency is reached which is considerably higher than that required for the surface effect. Although this conclusion was based on considerations which it is very difficult to make precise, it seems probable that near the long wave-length limit, and in the high energies of the ejected electrons, the volume effect can be neglected entirely.

Mitchell[3] has criticized the work of Tamm and Schubin in some of its details without, however, changing the major conclusions. He also extended the treatment to the case of a potential barrier representing an image field. The first part of this paper will be devoted to the extension of Mitchell's treatment to the case in which the form of the potential barrier is not specifically given, and it will be shown that some conclusions about the barrier can be drawn from the observed currents.

The second part of the problem has been treated by Fowler and by DuBridge.[4] In these treatments various assumptions were made as to the probability of excitation of the electrons, and the assumptions were based to some extent on the possibility of integrating the resulting expressions. These assumptions have been analyzed and classified by Rudberg.[5] Mitchell also worked out this part of the problem on the basis of his results from the study of excitation probabilities, and showed a connection between the form of the transmission coefficient of the surface and the temperature dependence of the photo-current near the threshold. In the second part of this paper the distribution of energies normal to the surface will be calculated, and the dependence of this distribution on the form of the potential barrier will be discussed.

The third part will be concerned with the application of the theory to the experimental results, especially those described by Overhage in the accompanying paper. The fact that the distribution of normal energies measured by a retarding potential should, in the high energy region, be essentially independent of the cathode potential barrier makes it necessary to invoke some other factor to explain the observations. This factor is the potential barrier on the anode, and it is possible to draw some conclusions as to the transmission of this barrier from a consideration of the observed energy distribution.

PART I. PROBABILITY OF EXCITATION

In treating the surface photo-effect it will be assumed that the problem is essentially one-dimensional. This is justified by the fact that a change in electron energy parallel to the surface is subject to the restrictions of the volume photo-effect, and may be expected to require frequencies considerably higher than the ordinary threshold. It is also true that an absorption of energy in the motion parallel to the surface reduces the energy available normal to the surface. For both of these reasons this possibility can be neglected near the threshold. In addition it will be assumed that the potential inside the metal is constant, and that the periodic structure is unimportant. This, also, is to be justified on the basis of the selection rules for the volume effect and the restriction of the results to apply to the surface effect.

Consider then a one-dimensional potential field in which three regions are to be distinguished:

Region I	$x<0,$	$V(x)=-W_a,$
Region II	$0<x<x_0,$	$V(x)$ arbitrary,
Region III	$x_0<x,$	$V(x)=0.$

For regions I and III the stationary state wave

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[2] R. A. Millikan, Phys. Rev. **18**, 236 (1921).

[3] K. Mitchell, Proc. Roy. Soc. **A146**, 442 (1934); Proc. Camb. Phil. Soc. **31**, 416 (1935).

[4] R. H. Fowler, Phys. Rev. **38**, 45 (1931); L. A. DuBridge, Phys. Rev. **39**, 108 (1932).

[5] E. Rudberg, Phys. Rev. **48**, 811 (1935).

functions can be written down immediately. For $E_f > 0$,

$$\begin{aligned} &\psi_f{}^+ = e^{igx} + a_f e^{-igx}, \quad \psi_f{}^+ = b_f e^{ifx} \\ \text{and} \quad &\psi_f{}^- = a_f{}^* e^{igx} + e^{-igx}, \quad \psi_f{}^- = b_f{}^* e^{-ifx} \end{aligned} \tag{1}$$

form a set of independent solutions with

$$f^2 = (2m/\hbar^2)E_f, \quad \text{and} \quad g^2 = (2m/\hbar^2)(E_f + W_a).$$

The constants a_f and b_f could be evaluated for any specified form of the potential in region II. Also for $E_k < 0$, in region I

$$\psi_k = \alpha_k \cos(kx + B_k), \tag{1a}$$

where $k^2 = (2m/\hbar^2)(W_a + E_k)$ and B_k could be determined for a specified potential in region II.

The problem is now to find the perturbation of a given initial state u_k by a light wave whose vector potential is

$$\mathbf{A} = 2\mathbf{a} \cos 2\pi\nu(t + x \cos\vartheta/c), \tag{2}$$

where ϑ is the angle of incidence. If the resulting wave function is $u = u_k + v$, with $u_k = \psi_k e^{-i(E_k/\hbar)t}$, v satisfies the equation[6]

$$(\hbar^2/2m)\partial^2 v/\partial x^2 - (\hbar/i)(\partial v/\partial t) - Vv = -(\hbar e/imc)A_x \partial u_k/\partial x. \tag{3}$$

Following exactly the procedure of Mitchell leads to

$$v = (2\pi m/\hbar r)(k|a_x|r)^+ \psi_r{}^+ e^{-(i/\hbar)(E_k + h\nu)t} \tag{4}$$

for large values of x and t. r is the value of f for which

$$E_r = E_k + h\nu.$$

Corresponding to this value of v is a current, when $x > x_0$, given by

$$\begin{aligned} j_x &= (e\hbar/im)v^* \partial v/\partial x \\ &= (4\pi^2 me/\hbar r)|(k|a_x|r)^+|^2 |b_r{}^+|^2. \end{aligned} \tag{5}$$

On the assumption that the wave-length of the light is long compared with the thickness of the potential barrier, so that the vector potential may be treated as constant in the region which contributes to the integral, the matrix element is given by

$$(k|a_x|r)^+ = \frac{(e/mc)a_x r}{2\pi g(1 - |a_r|^2)} \int_{-\infty}^{\infty} dx \frac{d\psi_k}{dx} \times \{\psi_r{}^{+*} - a_r{}^* \psi_r{}^{-*}\}. \tag{6}$$

In region I from $x = -\infty$ to $x = 0$ the functions are known, and with a convergence factor as used by Mitchell the integration gives

$$-\frac{(1 - |a_r|^2)\hbar^2 k \alpha_k}{2mh\nu}\{ig \sin B_k + k \cos B_k\}.$$

The remainder of the integral can be transformed by using the properties of the functions as expressed in the differential equation. Take the equation for $\psi_r{}^{+*}$ and multiply it by $d\psi_k/dx$. Then differentiate the equation for ψ_k and multiply by $\psi_r{}^{+*}$. By subtracting the second from the first, integrating by parts, and using the original differential equation it can be shown that

$$(E_r - E_k)\int_0^\infty \psi_r{}^* \frac{d\psi_k}{dx} dx = \left\{(E_k + C)\psi_k \psi_r{}^* + (\hbar^2/2m)\frac{d\psi_k}{dx}\frac{d\psi_r{}^*}{dx}\right\}_{x=0}.$$

The quantity C is a mean value of the potential in the barrier defined by

$$C\int_0^\infty \frac{d}{dx}(\psi_k \psi_r{}^*)dx = -\int_0^\infty V(x)\frac{d}{dx}(\psi_k \psi_r{}^*)dx.$$

With the known values of the functions at $x = 0$ the matrix element is

$$(k|a_x|r)^+ = -(ea_x r/2\pi mch\nu g)(W_a - C)\cos B_k \alpha_k. \tag{7}$$

Inserting this value of the matrix element the current from this one initial state is

$$j_x = (e^2/\hbar c)(e/mc)(a_x/h\nu)^2 |\alpha_k|^2 \times |W_a - C|^2 \cos^2 B_k D(r)/g, \tag{8}$$

where the transmission coefficient

$$D(r) = (r/g)|b_r|^2.$$

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[6] The signs of this equation differ from those given by Mitchell because of the consistent use of the opposite convention for the sign of $\hbar/i$.

Let

$$|W_a-C|^2\cos^2 B_k D(r)/g=F(E_r,\nu)k(\hbar^2/2m). \quad (9)$$

The component parts of F are all functions of k and r, and so can be expressed as functions of E_r and ν.

The computation of $F(E_r, \nu)$ can always be carried out by suitable approximation methods if the potential is specified, although in using a W.K.B. approximation care must be taken not to neglect the reflection. For potential barriers made of discontinuities the function can be given exactly in relatively simple form. For a simple discontinuity region II shrinks to zero and

$$F(E_r,\nu)=4(W_a+E_r-h\nu)^{\frac{1}{2}}W_aE_r^{\frac{1}{2}}/\{(E_r+W_a)^{\frac{1}{2}}+E_r^{\frac{1}{2}}\}^2. \quad (9a)$$

For small values of E_r this varies as $E_r^{\frac{1}{2}}$ due to the form of the transmission coefficient. The variation of the other factors is of little importance.

In case the potential rises from $-W_a$ to $+B$ at $x=0$, and then drops to zero at $x=d$, the exact form of $F(E_r, \nu)$ is more complicated. In the important case in which the energy of the bound state is enough less than zero and the thickness of the barrier is not too small

$$F(E_r,\nu)=(W_a+B)^2(W-h\nu+E_r)^{\frac{1}{2}}D(E_r)/W_a(W_a+E_r)$$

with

$$D(E)=\frac{4(B-E)(E+W_a)^{\frac{1}{2}}E^{\frac{1}{2}}}{(B+W_a)B\cosh^2\{(2m/\hbar^2)(B-E)\}^{\frac{1}{2}}d-\{E^{\frac{1}{2}}(E+W_a)^{\frac{1}{2}}-B+E\}^2}. \quad (9b)$$

In each of these cases the behavior at $E_r=0$ is governed by the behavior of the transmission coefficient. In cases in which the potential does not vary too rapidly in the barrier the transmission coefficient will approach a finite value and the derivative will be finite. Under these circumstances the function $F(E_r, \nu)$ can be developed in a power series in E_r with coefficients which are functions of ν but can be expected not to vary too rapidly with it.

PART II. CALCULATION OF OBSERVED CURRENT

Equation (8) gives the current due to the one initial state in which the electron density is $|\alpha_k|^2$. To determine the total photocurrent it is necessary to insert the value of this density, which is given by the Fermi statistics, and to integrate over all of the initial states.

The Fermi distribution function gives the electron density as a function of the energy, and for strictly free electrons this can be expressed in terms of the quantity k. The free electron approximation is certainly very good for the alkalis, but to make some allowance for possible deviations from it let

$$E(k,k_y,k_z)=E(k^2+k_y^2+k_z^2)$$

such that if $k^2+k_y^2+k_z^2=s^2$, and $E(s_0^2)=h\bar{\nu}$,

$$s^2-s_0^2=\beta(E-h\bar{\nu})+\gamma(E-h\bar{\nu})^2, \quad (10)$$

where $h\bar{\nu}$ is the energy for which the Fermi function gives a probability of $\frac{1}{2}$. With the potentials used here $\bar{\nu}<0$. Eq. (10) imposes a condition of spherical symmetry on the energy which is probably satisfied in the region of importance. It may be regarded as the first part of a series expansion in which s^2 is expressed as a function of E. s^2 is expressed as a series in E rather than E as a series in s^2 in order that the required derivatives shall have a simple form.

Let

$$A=(he^3/8m^2c^2)(a_x/h\nu)^2,$$
$$w=\{E(k^2+\rho^2)-h\bar{\nu}\}/\kappa T,$$
$$y=\{E(k^2)-h\bar{\nu}\}/\kappa T,$$
$$\rho^2=k_x^2+k_y^2.$$

Consider first the case in which the saturation current is observed. All of the electrons which penetrate the potential barrier of the cathode will be collected and the total current can be obtained by integrating over all of the electrons with positive E_r. Thus

$$J=2A\kappa T\int_0^\infty kdkF(E_r,\nu)\int_y^\infty \frac{(\beta+2\gamma\kappa Tw)dw}{(e^w+1)}. \quad (11)$$

The integration over k can be transformed to an integration over $E(k^2)$ by Eq. (10) and then to one over E_r, so if

$$S_1(y)=\int_y^{\infty} w\,dw/(e^w+1),$$

$$J=A\kappa T\int_0^{\infty} dE_r F(E_r,\,\nu)(\beta+2\gamma\kappa Ty)\times\{\beta\log(1+e^{-y})+2\gamma\kappa TS_1(y)\}. \qquad (12)$$

The form of this integral will clearly depend upon the form of the function $F(E_r,\,\nu)$ which is not known and which depends upon the surface potential barrier, especially through the transmission coefficient D. In the case of an image field this transmission has a finite value at $E_r=0$. In the case of the discontinuous potentials mentioned above the transmission vanishes at $E=0$ and increases with $E_r^{\frac{1}{2}}$ above it until in the second case the exponential factor becomes dominant. It seems probable that the increase with $E^{\frac{1}{2}}$ is largely due to the nonphysical discontinuities introduced into the assumed potential, and that in most cases a form of $F(E_r,\,\nu)$ can be expected which can be expanded in a Taylor series above the point $E_r=0$. At least let us assume this to be the case and let

$$F(E_r,\,\nu)=F(0,\,\nu)+E_rF'(0,\,\nu)+\cdots. \qquad (13)$$

From the conservation of energy

$$E_r/\kappa T=y+(h\nu+h\bar{\nu})/\kappa T=y+x,$$

where $$x=+(h\nu+h\bar{\nu})/\kappa T.$$

Eq. (12) then becomes

$$J=A(\kappa T)^2\int_{-x}^{\infty} dy\{F(0,\,\nu)+\kappa T(y+x)F'(0,\,\nu)+\cdots\}(\beta+2\gamma\kappa Ty)\{\beta\log(1+e^{-y})+2\gamma\kappa TS(y)\}$$
$$=A(\kappa T)^2\{I_0+\kappa TI_1+\cdots\} \qquad (14)$$

with $$I_0=\beta^2F(0,\,\nu)\int_{-x}^{\infty} dy\log(1+e^{-y})=\beta^2F(0,\,\nu)\Phi_0(x),$$

$$I_1=\beta^2F'(0,\,\nu)(\Phi_1(x)+x\Phi_0(x)\}+2\beta\gamma F(0,\,\nu)\{\Phi_1(x)+\Theta_1(x)\},$$

$$\Phi_1(x)=\int_{-x}^{\infty} y\,dy\log(1+e^{-y}),$$

$$\Theta_1(x)=\int_{-x}^{\infty} S_1(y)dy.$$

In the other case in which only part of the electrons are collected because of the use of a retarding field it is necessary to integrate not from $E_r=0$, but from the minimum value of E_r with which an electron can reach the anode. Let this minimum value be Ve. It is also necessary to take account of the reflection at the surface of the anode since its potential barrier also will, in general, transmit only a part of the electrons. Let $R(E_r-Ve)$ be the anode transmission coefficient, and assume that this can be expanded about the point $E_r=Ve$. Then the observed current will be

$$J=A(\kappa T)^2\int_{-x'}^{\infty} dy\{R(0)+R'(0)(y+x')+\cdots\}\times\{F(0,\,\nu)+\kappa T(y+x)F'(0,\,\nu)+\cdots\}\times(\beta+2\gamma\kappa Ty)\{\beta\log(1+e^{-y})+2\gamma\kappa TS_1(y)\}$$
$$=A(\kappa T)^2\{I_0'+\kappa TI_1'+\cdots\} \qquad (15)$$

where $I_0'=\beta^2R(0)F(0,\,\nu)\Phi_0(x')$,

$$I_1'=\beta^2\{R(0)F'(0,\,\nu)+R'(0)F(0,\,\nu)\}\times\{\Phi_1(x')+x'\Phi_0(x')\}+\beta^2R(0)F'(0,\,\nu)(x-x')\Phi_0(x')+2\beta\gamma R(0)F(0,\,\nu)\{\Phi_1(x')+\Theta_1(x')\},$$

and $$x'=+(h\nu+h\bar{\nu}-Ve).$$

The various integrals in Eqs. (14) and (15) can be easily evaluated after expansion of the integrands in series. The function Φ_0 is just that given by Fowler. For $x<0$,

$$\Phi_1(x)=-x(e^x-e^{2x}/4+e^{3x}/9-\cdots)+(e^x-e^{2x}/8+e^{3x}/27-\cdots)$$

and for $x>0$,

$$\Phi_1(x)=-x^3/3+x(e^{-x}-e^{-2x}/4+e^{-3x}/9-\cdots)+(e^{-x}-e^{-2x}/8+e^{-3x}/27-\cdots).$$

TABLE I

x	$\Phi_0(x)$	$\Phi_1(x)$	$\Phi_1+x\Phi_0$	LOG $(\Phi_1+x\Phi_0)$
−5	0.00673	0.04039	0.00674	−2.171
0	0.8225	0.9014	0.9014	−0.045
5	14.138	−41.660	29.030	+1.463
10	51.645	−333.33	183.12	+2.263
15	114.15	−1125.00	587.3	+2.769
20	201.65	−2666.67	1366.3	+3.135
25	314.14	−5208.3	2645.2	+3.422
30	451.64	−9000.0	4549.2	+3.658

A few values of these functions are given in Table I.

PART III. APPLICATION TO EXPERIMENTAL RESULTS

Equations (14) and (15) indicate a number of possible forms of observed current as a function of the variable x. The form to be expected in any particular case depends upon the characteristics of the cathode and the anode as expressed in the functions $F(E_r, \nu)$ and $R(E_r-Ve)$. By comparison of the observed curves with the various theoretical functions one can attempt to draw some conclusions as to the surfaces.

The work of Overhage described in the accompanying paper is characterized by two facts. First, the observations are clearly not to be fitted to the curve $\Phi_0(x)$. Second, the curves for different frequencies can be superimposed with considerable accuracy. These two facts can both be accounted for on the assumption that $R(0)=0$. This leads to the equation

$$J=A(\kappa T)^3\beta^2R'(0)F(0,\nu)\times\{\Phi_1(x')+x'\Phi_0(x')\}. \quad (16)$$

In this expression all of the dependence upon ν is in A and $F(0, \nu)$ which occur in the multiplicative factor. When the logarithms of both sides are taken this dependence upon ν will affect the shift necessary for each frequency, but will not at all affect the shape of the curve. Fig. 1 shows the theoretical curve of $\log\{\Phi_1(x)+x\Phi_0(x)\}$ plotted against x. Superposed on it are points taken from Overhage's composite curve of $\log I$ against $Ve/\kappa T$ after the necessary horizontal and vertical displacements have been made. The agreement is sufficiently good to give one some confidence in the correctness of the suggested explanation. Furthermore, in view of the fact that the anode work function was apparently considerably reduced by a very thin layer of sodium on it, it is not surprising that the transmission coefficient of the barrier should approach zero gradually rather than stopping suddenly.

If it were possible to keep the surfaces of the electrodes, and the work functions, unchanged during a change of temperature, the temperature dependence at the threshold should show a variation with T^3 rather than with T^2. Although an observation of this point would be very interesting it probably presents grave experimental difficulties because of the tendency of a complex surface to change with the temperature.[7] Mitchell indicated that the temperature dependence might be expressible in terms of $T^{\frac{1}{2}}$ on the ground that the transmission coefficient should be expressed as a series in r rather than E. Investigation of this point would certainly throw some light upon the nature of the surface.

Although the agreement between the experimental points and the theoretical curve in Fig. 1 is quite good, there is a definite systematic

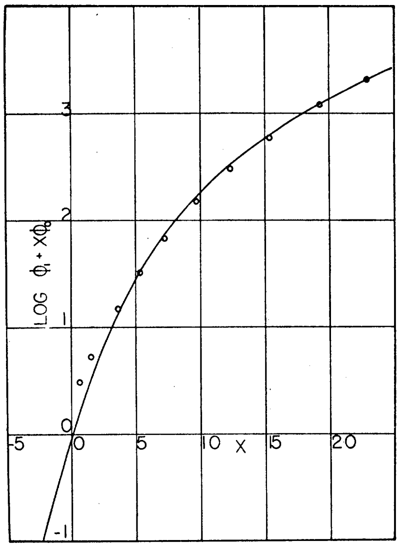

FIG. 1. The solid curve is $\log\{\Phi_1(x)+x\Phi_0(x)\}$ plotted against x. The points are taken from the composite curve given by Overhage in the accompanying paper.

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[7] In a paper which has just appeared, Cashman has shown that the observed temperature variation of the photo-current at the threshold is not of the type required by any theory, and has attributed the difference to a temperature dependence of the work function. Whether or not this is a complete explanation, it is a factor which must certainly be considered, and which will complicate the interpretation of the observed currents. Phys. Rev. **52**, 512 (1937).

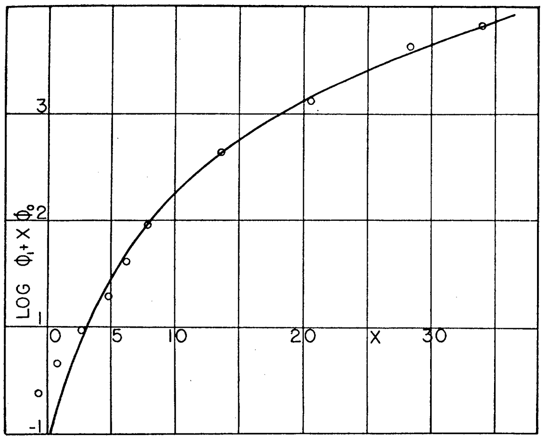

FIG. 2. The curve is log $\{\Phi_1(x)+x\Phi_0(x)\}$ plotted against x. The points are taken from those published by Mann and DuBridge for sodium.

discrepancy, especially at the lower end. This is, of course, the region in which the measured currents are very small and where some experimental error is to be expected. If, however, this discrepancy is regarded as significant, it indicates that the terms in the next power of κT are important. In fact, if to the function $\{\Phi_1(x)+x\Phi_0(x)\}$ there is added $(1/10)\int_{-x}^{\infty}(y+x)\log(1-e^{-y})dy$, the agreement can be made almost perfect. It is questionable, however, whether the data is such as to justify so detailed a treatment.

Other observations on the photocurrent from sodium which show a lack of agreement with the simple theory have been published by Mann and DuBridge.[8] Since they were observing the saturation current as a function of frequency Eq. (14) should apply. Fig. 2 shows log $\{\Phi_1+x\Phi_0\}$ plotted against x and compared with some points taken from their published curve. The agreement is very similar to that in Fig. 1 and would indicate that the transmission coefficient of the sodium surface which they were using increased from zero with the first, and possibly a small contribution from the second, power of the energy. Correspondingly the current at the threshold should have been roughly proportional to T^3.

In these two cases it is unnecessary to invoke the constant γ to satisfy the observations. This is certainly what was to be expected in the case of the alkalis, although for some other substances it may be necessary. The value of β must then be $(2m)^{\frac{1}{2}}/\hbar$. One can also conclude that in the considerable number of substances for which the observed currents have been shown to follow the Fowler curve, the transmission coefficient is roughly constant above the threshold. This seems to be true rather generally for the heavy metals in very pure condition.

It thus seems possible to determine from the energy distribution of the photoelectrons and from the spectral distribution of the photocurrent something about the nature of the potential barriers on the cathode and on the anode. It may also be possible to study the effect of alkalis, or of oxides, on the surfaces of pure metals by observing the change of the distributions with time.

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[8] Mann and DuBridge, Phys. Rev. **51**, 120 (1937).