A FURTHER EXPERIMENTAL TEST OF FOWLER'S THEORY OF PHOTOELECTRIC EMISSION

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Abstract

Fowler's theory of photoelectric emission is discussed from the viewpoint of the experimental physicist and several significant consequences of the theory in analyzing experimental data pointed out. A new graphical method of testing the theory is suggested. This method makes it possible to determine the "true" photoelectric threshold of a surface from photocurrent-temperature curves taken at a single incident frequency, eliminating the necessity of measuring relative intensities of spectral lines. The method is applied to new experimental data on palladium and to Morris' data on gold and found to be completely successful, thus furnishing additional verification of Fowler's theory.

R. H. FOWLER[1] has recently made an important contribution to the theory of the photoelectric effect in metals by deriving an equation for the specific photoelectric emission from a metal surface as a function of the frequency of the incident light and the temperature of the surface. He has devised an ingenious graphical method of testing the theory and has shown that it is in excellent agreement with the best experimental results. The same graphical method is also used to determine from experimental results the true photoelectric threshold of the metal. The purpose of the present paper is to discuss some of the experimental implications of Fowler's theory and to suggest another method of testing the theory and determining the threshold. The method is an obvious variation of the one proposed by Fowler, but it is of considerable interest in itself and has been found by the author to be extremely useful in analyzing experimental data.

I. Discussion of Fowler's Theory

Fowler's assumptions are: (1) that the electrons within a metal obey the Fermi-Dirac statistics and (2) that the number which will be ejected by unit energy of absorbed light of any frequency ν is proportional to the number within the metal which have energies normal to the surface such that, when augmented by the energy $h\nu$, they are sufficient to surmount the surface potential step χ_0. Fowler was able greatly to simplify the theory by considering only the effects of incident frequencies which do not differ greatly from the threshold frequency ν_0. This restriction eliminates the necessity of considering such uncertain quantities as transition probabilities of electrons through surface potential barriers, for these introduce terms which can be considered essentially constant over small frequency ranges. On the other

[1] R. H. Fowler, Phys. Rev. **38**, 45 (1931).

hand the restriction is not a serious one from the experimental viewpoint for, except for the alkali metals, the frequencies available experimentally lie as a rule within 30 percent of the threshold, and over this range the theory is reasonably exact. The final equation obtained for the photoelectric current I excited in a metal surface at the temperature T by unit intensity of absorbed light of frequency ν is

$$\log_{10} I/T^2 = B + \Phi(\mu), \tag{1}$$

where $B = $ constant, independent of ν and T,

$$\mu \equiv h(\nu - \nu_0)/kT,$$

and $\Phi(\mu)$ is a universal function of μ given by

$$\Phi(\mu) = \log_{10}(e^\mu - e^{2\mu}/2^2 + e^{3\mu}/3^2 - \cdots) \text{ for } \mu \leqq 0, \tag{2}$$

$$\Phi(\mu) = \log_{10}(\pi^2/6 + \tfrac{1}{2}\mu^2 - [e^{-\mu} - e^{-2\mu}/2^2 + e^{-3\mu}/3^2 - \cdots]) \text{ for } \mu \geqq 0, \tag{3}$$

Values of $\Phi(\mu)$ for a series of values of μ are listed in Table I, and these are plotted in the curve shown in Fig. 1.

TABLE I. *Values of Fowler's function* $\Phi(\mu)$.

μ	$\log_{10}|\mu|$	$\Phi(\mu)$	μ	$\log_{10}|\mu|$	$\Phi(\mu)$
−8.0	+0.903	−3.475	+2.0	+0.301	+0.546
−6.0	0.778	−2.606	3.0	0.477	0.785
−5.0	0.699	−2.171	4.0	0.602	0.983
−4.0	0.602	−1.739	5.0	0.699	1.150
−3.0	0.477	−1.308	6.0	0.778	1.293
−2.5	0.398	−1.095	8.0	0.903	1.527
−2.0	0.301	−0.884	10.0	1.000	1.713
−1.5	0.176	−0.674	12.0	1.079	1.866
−1.0	0.000	−0.469	14.0	1.146	1.998
−0.5	−0.301	−0.268	16.0	1.204	2.113
−0.2	−0.699	−0.160	20.0	1.301	2.305
0.0	−∞	−0.085	25.0	1.398	2.497
+0.2	−0.699	−0.015	30.0	1.477	2.655
0.4	−0.398	+0.055	35.0	1.544	2.788
0.6	−0.222	0.125	40.0	1.602	2.904
1.0	0.000	0.249	50.0	1.699	3.097
1.5	+0.176	0.400			

Fowler's method of testing Eq. (1) is as follows: Observations are taken of the photoelectric current per unit intensity as a function of frequency, for a metal surface at a fixed temperature T. A plot is made of $\log I/T^2$ as a function of $h\nu/kT$. This observed curve should be of the form of the theoretical curve of Fig. 1, and should, after a shift parallel to itself, coincide with it. The vertical component of this shift is unimportant, since it involves only the constant B and will depend on the units in which the current and light intensity are measured. The horizontal component, however, should be equal to $h\nu_0/kT$, from which ν_0 may be determined. Fowler showed in this way that the theory was in excellent agreement with the observations of Winch,[2] Morris[3] and Cardwell[4] on Ag, Au, and Ta, respectively, while it has been

[2] R. P. Winch, Phys. Rev. **37**, 1269 (1931).

[3] L. W. Morris, Phys. Rev. **37**, 1263 (1931).

[4] A. B. Cardwell, unpublished.

shown in the previous paper in this issue of the Physical Review[5] that it is also in good agreement with the results of DuBridge and Roehr on palladium.[6]

The success of Fowler's theory makes it imperative to inquire further into its significance and its consequences. We find at once that, while it introduces no radically new ideas as to the nature of the photoelectric process itself, it nevertheless gives a quantitative interpretation of many experimental facts in the field of photoelectricity which have been a puzzle for many years. At the same time, because of its simplicity in form, it is exceedingly useful in analyzing and coordinating experimental data, and in serving as a guide to further research. There are several features of the theory which are of par-
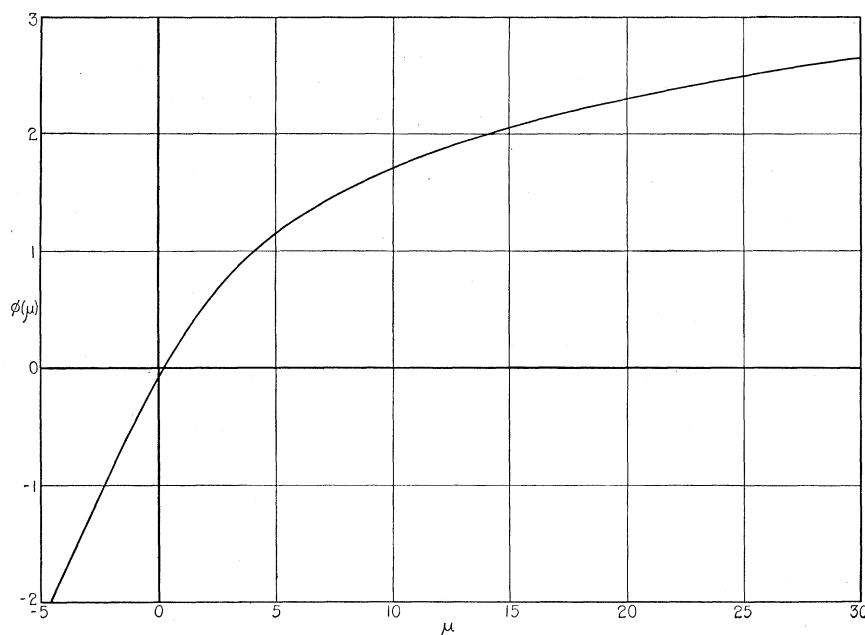

Fig. 1. Fowler's theoretical curve, $\Phi(\mu)$ vs. μ.

ticular interest to the experimentalist, and which therefore deserve further discussion.

1. The fact that the quantity log I/T^2 turns out to be a *universal* function of μ is in itself of considerable interest since it will very greatly simplify the analysis and comparison of experimental results. In view of the wide variety in the forms of ordinary spectral distribution curves (I vs. ν) it is a result which would scarcely have been expected.

2. The threshold frequency ν_0 is defined by Fowler from the equation,

$$h\nu_0 = \phi_0 e = \chi_0 - \epsilon^*$$ (4)

where ϵ^* is the maximum kinetic energy of the electrons at absolute zero on

[5] L. A. DuBridge and W. W. Roehr, Phys. Rev. 39, 99 (1932).

[6] G. N. Glasoe (Phys. Rev. 38, 1490 (1931)) also finds an agreement with his results (for a single temperature) on Fe and Ni. See also A. H. Warner, Phys. Rev. 38, 1871 (1931).

the Fermi statistics, and ϕ_0 is the surface work function. It is evident that ν_0 is *not* the threshold obtained by the ordinary method of extrapolating spectral distribution curves to the axis, for, as can be seen from Eq. (3), for $T >$ 0°K the current I does not fall to zero at $\nu = \nu_0$, but approaches zero asymptotically as ν decreases. *Hence there is no such thing as a sharply defined threshold at any temperature above* 0°K. At this temperature, however, I is proportional to $(\nu - \nu_0)^2$ so that ν_0 is the threshold at absolute zero. Since ν_0 is a real characteristic of the surface it may be called the *true* threshold, while ϕ_0 is the *true* work function. (ϕ_0 should be equal to the thermionic work function, since this is also defined by Eq. (4).) Fowler's theory gives a method by which the true threshold ν_0 may be determined from measurements made at ordinary temperatures.

3. Fowler's theory has greatly clarified the question of the temperature variation of the photoelectric effect, a problem which has been extensively investigated. It is evident that it is now meaningless to speak of the "temperature variation of the photoelectric threshold," for the *true* threshold is not temperature dependent, while the *apparent* thresholds obtained by extrapolation methods do not have sufficient quantitative significance to permit of exact discussion.[7] The question as to the temperature variation of photocurrents due to monochromatic light has, however, taken on added interest. It is well known that the early experiments showed that, over small temperature ranges, the photoelectric currents excited by *unresolved* light were nearly independent of temperature, while in a number of more recent experiments, taken over a wider temperature range, a definite increase of photocurrent with temperature has been observed. Ives[8] was the first to show that the increase is greater for light of longer wave-length. The only quantitative experiments with monochromatic light are those of Winch,[2] Morris,[3] and DuBridge and Roehr,[5] and these, as will be shown, are in complete agreement with Fowler's theory. According to this theory the temperature variation depends greatly on the incident frequency. Thus for $\nu = \nu_0$, I is proportional to T^2. For larger frequencies the variation is much slower and becomes almost inappreciable for light which is 200A or more on the short wave-length side of the threshold. For ν less than ν_0, on the other hand, the variation is extremely rapid, due to the exponential terms in Eq. (2). It is significant that *the temperature changes observed experimentally are entirely accounted for by the increase in thermal energy of the electrons*, without the necessity of attributing them to changes in the surface itself, such as thermal expansion, etc.

4. The lack of sharpness in the threshold at temperatures above 0°K in-

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[7] This is of particular interest in connection with the recent discussion on the relation of the temperature variation of the threshold to the value of the thermionic coefficient A. (See L. A. DuBridge, Proc. Nat. Acad. Sci. **14**, 788 (1928); P. W. Bridgman, Phys. Rev. **31**, 90 (1928); K. F. Herzfeld, Phys. Rev. **35**, 248 (1930); J. A. Becker and W. H. Brattain, Phys. Rev. **37**, 462 (1931)). Evidently abnormal values of A can *not* be ascribed to a temperature coefficient of ν_0, since the *apparent* changes in ν_0 are due only to the thermal energies of the electrons and not to a real change in work function.

[8] H. E. Ives, J. O. S. A. **8**, 551 (1924); H. E. Ives and A. L. Johnsrud, J. O. S. A. **11**, 565 (1925).

volves also a lack of sharpness in the *maximum velocity* of the emitted electrons. And this means that the Einstein equation can be expected to hold exactly only at very low temperatures. This is an exceedingly important result, and one which requires further theoretical and experimental examination. It is a matter of good fortune that at room temperature the lack of sharpness in the threshold is not sufficiently marked to produce *serious* errors in the determinations of ν_0 by extrapolation. The lack of sharpness is *appreciable*, however, and *does* become serious at high temperatures. It remains to be seen how great are the errors involved in the usual method of determining *maximum velocities* of emission.

5. Finally it should be mentioned that the variation of the photocurrent with frequency and temperature predicted by Fowler's theory are due directly to the characteristics of the Fermi distribution of velocities among the electrons, and to nothing else. The success of the theory thus constitutes one of the most direct and most convincing tests yet obtained of the applicability of the Fermi-Dirac statistics to electrons in metals.

II. ANOTHER METHOD OF DETERMINING ν_0

Fowler's method of analyzing photoelectric observations consists in measuring I as a function of ν for a fixed value of T, and then plotting $\log I/T^2$ against $h\nu/kT$. By taking observations at other values of T one obtains a series of "isothermal" curves, and from the horizontal shifts required to make these curves fall on the theoretical curve, ν_0 is determined. There is, however, another obvious method of using Fowler's equation for the analysis of photoelectric observations, which, besides being of interest in itself, offers a number of advantages over Fowler's own method. By making use of this new method it is possible to determine ν_0 from measurements made at a *single frequency* of incident light, and this eliminates the necessity of measuring the relative intensities of spectral lines.

The method is as follows: Instead of plotting Fowler's function $\Phi(\mu)$ against μ, plot it as a function of $\log |\mu|$. The necessary data are given in Table I and the curve obtained is shown in Fig. 2. This curve consists of two branches, one for positive and one for negative values of μ. We will confine our attention for the present to the positive branch. Now suppose that for incident light of a fixed frequency $(\nu > \nu_0)$ we observe the photoelectric current I as a function of the temperature of the emitting surface. We thus obtain an "isochromatic" instead of an "isothermal" run. If the observations are plotted in the form $\log I/T^2$ against $\log 1/T$ $(= -\log T)$ we obtain a curve which, after a shift parallel to itself, should coincide with the theoretical curve shown in Fig. 2. The vertical component of the shift is again unimportant. It will involve the constant B, and will depend on the units in which I is measured. It will depend also on the intensity of the incident light, since in this case it is not necessary to reduce I to unit intensity. The horizontal component of the shift, however, is equal to $\log h(\nu - \nu_0)/k$, because $\log \mu = \log[h(\nu - \nu_0)/k] - \log T$. Hence, knowing ν, we may determine ν_0 at once. It is evident that this process is quite analogous to that of determining the

"characteristic temperature" of a substance from specific heat data by plotting c_v against $\log T$. The quantity $h(\nu - \nu_0)/k$ in the present case is, in fact, a sort of characteristic temperature for the particular surface and the particular frequency of light used.

Let Δ be the horizontal shift required to bring the observed and theoretical curves into coincidence, and set $\log \theta = \Delta$. Then we should have,

$$h(\nu - \nu_0)/k = \theta.$$

In actual practice we usually desire to determine the work function ϕ_0 of the surface in volts. Then $\phi_0 e = 300 h\nu_0$. Let V be the voltage-equivalent of the frequency used, so that $Ve = 300 h\nu$. Then we should have
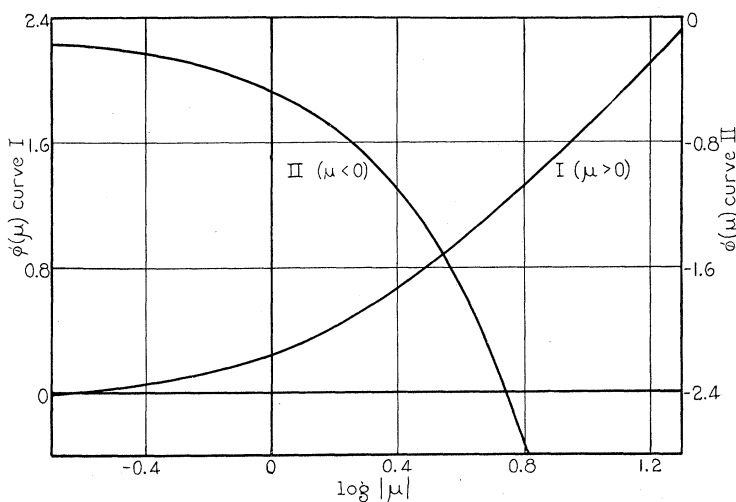
$$e(V - \phi_0)/300k = \theta.$$

Fig. 2. Fowler's theoretical curve, $\Phi(\mu)$ vs. $\log |\mu|$.

Whence,

$$\phi_0 = V - 300k\theta/e$$
$$= V - (8.61 \times 10^{-5})\theta.$$

(5)

The results of analyzing the experimental data in this way will be presented below, and it is shown that the method is completely successful. It is evident that this method of determining ϕ_0 has a number of distinct advantages over the previous one. In the first place, as has been pointed out, it makes possible for the first time the determination of ϕ_0 from measurements made at a single frequency. By taking several isochromatic curves at different frequencies, several determinations of ϕ_0 can be made, which, it has been found, agree within experimental error. Furthermore, in plotting these different curves it is not necessary to reduce I to unit intensity of absorbed light, for this factor would simply result in an additional vertical shift of each curve. (If I were reduced to unit intensity all curves would have the same vertical shift, but this does not assist materially in the "fitting" process.) It is

well known that measurements of the intensities of spectral lines are trouble-some at best and for weak lines in the far ultraviolet are exceedingly difficult to obtain accurately. A method which eliminates the necessity of making such measurments will be of interest to every experimentalist in this field. It is only necessary to insure that the intensity of the light remains constant during each run.

Another advantage of this method lies in the fact that the quantity directly determined from experiment is not ν_0 but $(\nu - \nu_0)$. Hence, as can be seen from Eq. (5), an error in determining θ makes a much smaller error in ϕ_0, since the second term is much smaller than the first and since V is usually known with considerable accuracy. Theoretically, therefore, this method is capable of high precision in determining ϕ_0. In actual practice, however, it was found that the precision of the two methods was about the same, due to the fact that small errors in determining $\log \theta$ give much larger errors in θ itself.

Finally there should be mentioned several sources of error which must be guarded against in analyzing observations by either of the two methods. In the first place, it has been assumed that there is a fixed ratio between the amount of light absorbed by the surface and the amount incident upon it, so that we do not need to distinguish between incident and absorbed energy. This will not be true if the reflectivity of the surface varies either with the fre-quency or with the surface temperature. A variation with *temperature* will only introduce different vertical shifts in the *isothermal* curves but will change the shape of the *isochromatic* curves and thus introduce an error in determin-ing ϕ_0. Changes with *frequency*, on the other hand, will only affect the vertical shift of the *isochromatic* curves, but will introduce an error in the *isothermals*. Fortunately, for the metals which have been studied, the reflectivity does not vary appreciably with either ν or T, but this possibility must be kept in mind, and if necessary corrected for. In this respect the isochromatic method of analysis has a slight advantage, since changes of reflectivity with tem-perature are more easily measured (by Winch's method[2]) than changes with frequency. (Care must be taken, of course, that the specimen does not warp or sag due to its thermal expansion so as to change the amount of light inci-dent upon it.)

It will be noted that the lower end of the curve of Fig. 1 and the upper end of curve I of Fig. 2 are quite accurately linear. Hence if the range covered by the observations falls on one of the linear portions, no unique fit is pos-sible and the threshold cannot be determined with certainty. The most ac-curate fitting of isothermal curves can thus be made in the region of low tem-peratures and high frequencies (i.e., ν considerably above ν_0), while for the iso-chromatic curves the most accurate results are obtained with high tempera-tures and low frequencies (ν near ν_0).

III. EXPERIMENTAL TESTS

The new method of testing Fowler's theory and determining the true work function was applied to the data on palladium obtained by the author

and Mr. W. W. Roehr (see previous paper) and to the data on gold published by Morris.[3] The latter set of data is the only one previously published in a form sufficiently complete to enable the necessary calculations to be made. The results for clean palladium have been plotted in Fig. 3, in which the experimental points have already been shifted by the amount necessary to make the individual observed isochromatic curves fall on the theoretical curve. The details of experimental procedure have been described in the previous paper, and the observations used here are the same ones represented by the curves of Fig. 2 of that paper. Points are shown for six different mercury arc lines on the short wave-length side of the threshold, and the temperature range covered in each run was from 305°K to 1070°K. The mag-
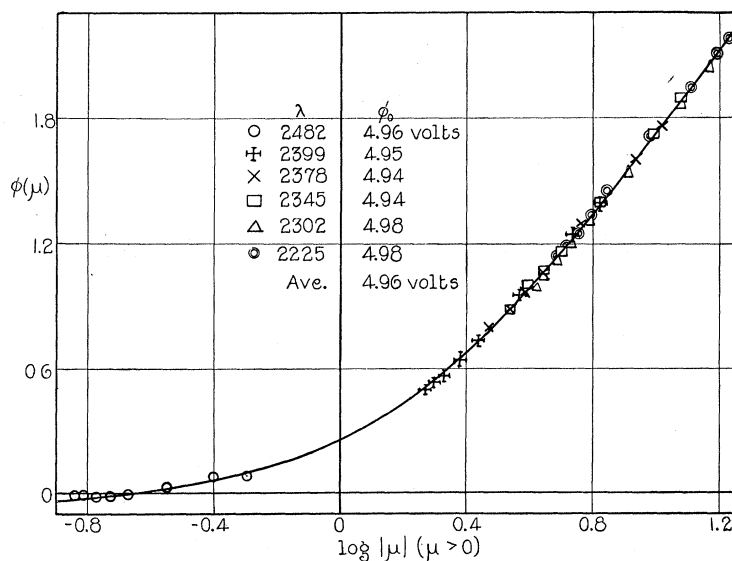

Fig. 3. Analysis of data for clean Pd.

nitudes of the horizontal shift ($\log \theta$) and of ϕ_0 for each wave-length are given in Table II. It is seen that the maximum deviation from the mean value of ϕ_0 is of the order of 0.5 percent, which is well within experimental error. The mean value is also in excellent agreement with the value 4.97 volts, obtained by analyzing data for the same specimen by Fowler's method.

TABLE II. *Analysis of data for clean palladium.*

λ(A)	V (volts)	$\log \theta$	ϕ_0 (volts)	λ_0 (A)
2225	5.549	3.75	4.98	2482
2302	5.363	3.65	4.98	2482
2345	5.265	3.56	4.94	2502
2378	5.192	3.47	4.94	2502
2399	5.146	3.36	4.95	2495
2482	4.972	2.19	4.96	2490
		Average	4.96	2491

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A similar plot of the data for palladium which had not been thoroughly outgassed, but which was in a fairly stable state, is shown in Fig. 4, and Mor-
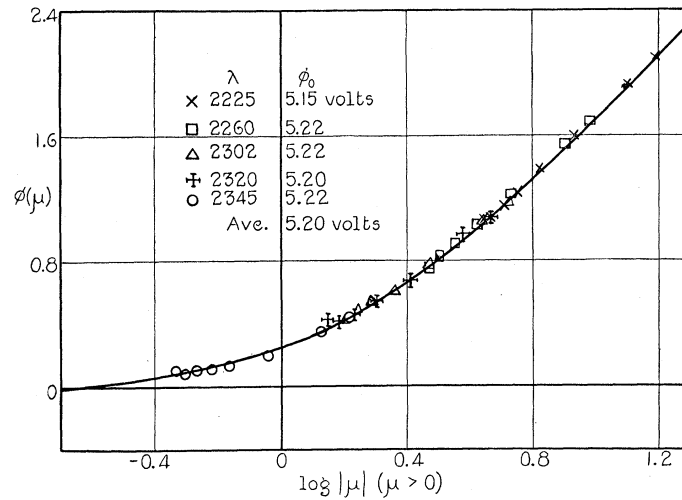

Fig. 4. Analysis of data for partially outgassed Pd.

ris' data for gold are shown in Fig. 5. It is seen that again an excellent fit with the theoretical curve is obtained and that the values of ϕ_0 are also in good
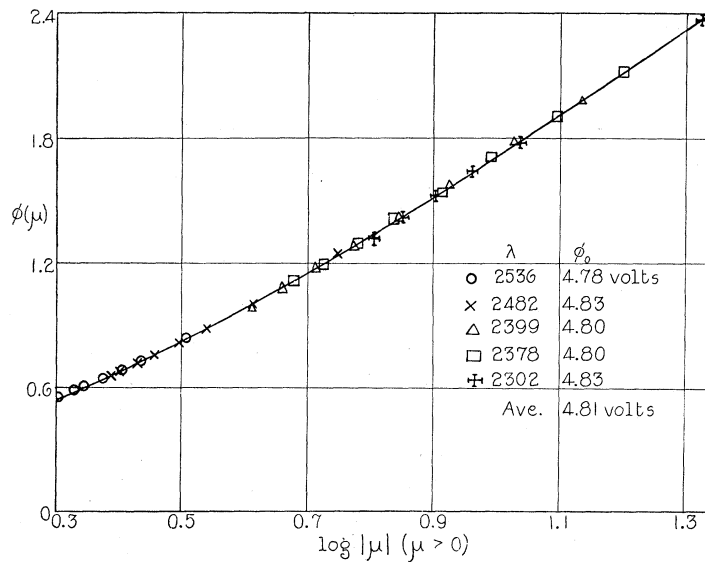

Fig. 5. Analysis of data for gold (Morris).

agreement. In the case of gold the average value of ϕ_0 obtained by this method (4.81 volts) is to be compared with the value 4.90 volts obtained by Fowler from his analysis of Morris' data. The discrepancy of about two percent might

easily be due to the errors involved in reading numerical values from the published curves. Also it was not certain that Morris' isochromatic runs were taken under exactly the same conditions as to freedom from gases as the isothermal curves used by Fowler.

Nothing has so far been said about the negative branch of the theoretical curve shown in Fig. 2. It is obvious that observations taken for a frequency which is on the long wave side of the true threshold ($\mu < 0$) should fall on this branch. Measurements in this region, however, are difficult to obtain accurately, owing to the smallness of the currents themselves, and to the relatively large fraction of these currents which may be due to stray light of shorter wave-lengths. Nevertheless, in a few cases reliable runs were obtained
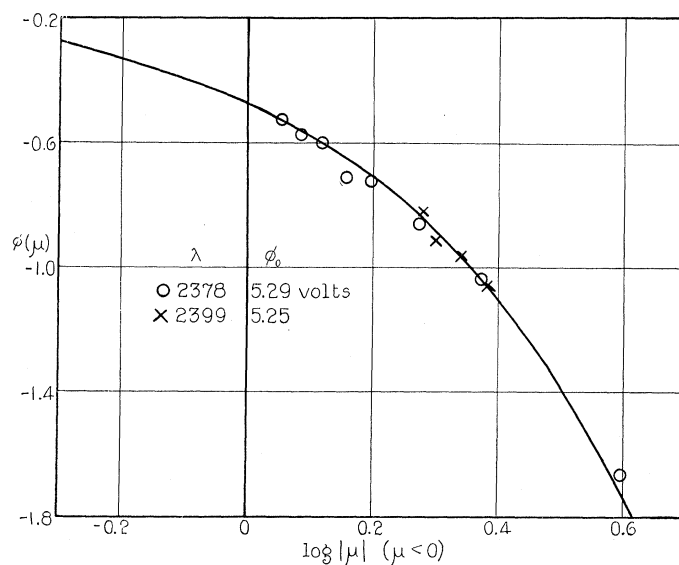

Fig. 6. Plot of data for $\nu < \nu_0$.

for one or two wave-lengths beyond the threshold, and the results are shown in Fig. 6. These runs were obtained at the same time as those shown in Fig. 4. The agreement, while not as good as before, is within experimental error, and the value of the work function agrees within about one percent with that obtained for shorter wave-lengths. While it is probably not practicable to use observations taken for $\nu < \nu_0$ in accurate determinations of ν_0, they nevertheless in this case furnish an additional experimental verification of the theory.

IV. CONCLUSION

It appears from the curves shown above and from those shown in Fowler's paper that Fowler's theory is in complete quantitative agreement with experiment, whether the isothermal or the isochromatic method of analysis be employed. His theory therefore marks a very great step forward in our understanding of photoelectric processes. It is particularly fortunate that Fow-

ler has put his theory in a form which is both understandable and useful to the experimental physicist in analyzing his data, and it may be expected to play an important role in future experimental studies.