THE ANALYSIS OF PHOTOELECTRIC SENSITIVITY CURVES FOR CLEAN METALS AT VARIOUS TEMPERATURES

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Abstract

An elementary theory is developed for the effect of temperature on the photoelectric sensitivity of a clean metal near the threshold. It is shown that the results observed by various workers for silver, gold, tantalum, tin, and potassium can be fairly completely accounted for by the effect of the temperature on the number of electrons available for extraction according to the distribution law of Sommerfeld's theory of metals. This is in agreement with the conclusions of Lawrence and Linford based on much less extensive data. A graphical method is given enabling the whole of the observed curves near the threshold for all temperatures to be used in determining the threshold itself thus avoiding an arbitrary extrapolation to zero current. At present the fundamental theory of the effect survives in two forms, both of which are used as alternatives here, with nearly equal success. Until one or the other can be eliminated it is not possible to determine thresholds closer than about 1 percent.

§1. INTRODUCTION

A SERIES of studies have recently been made of the photoelectric sensitivity of very carefully cleaned metal surfaces to very carefully monochromatized light, by a number of workers in the Department of Physics of the University of Wisconsin. Detailed accounts of this work, embodying results which have been on hand here for over a year have been or will be published elsewhere in this journal. The experiments establish with considerable accuracy the relative number of electrons ejected from the metal, per quantum of light absorbed¹ as a function of the frequency of the light and the temperature of the metal. The precautions required in rendering the light sufficiently monochromatic and the surface sufficiently clean are exceedingly elaborate and cannot be discussed here.² They are such that one can only suppose, at least as a natural first approximation, that the observed curves do really yield to us a true representation of the ideal photoelectric sensitivity of the *clean* metal at various temperatures to *monochromatic* light of various frequencies. Typical curves for silver³ and gold⁴ are shown in Fig. 1, and for tantalum⁵ in Fig. 2.

² Besides the various authors' own papers quoted below, a general account has been given by Mendenhall, Science **73**, 107 (1931).

³ Winch, Phys. Rev. 37,1263 (1931).

⁴ Morris, Phys. Rev. 37,1269 (1931).

⁵ Cardwell, Private communication.

¹ The experiments actually determine the current per unit incident light intensity and are controlled so as to detect any change of reflection coefficient as a function of the temperature. No significant changes occurred for the small frequency range in which we are here interested; therefore there is no need to distinguish between electrons per quantum absorbed and current per unit incident intensity.

It is at once clear from these curves that there is no sharp threshold value of ν_0 ; especially at the higher temperatures the photoelectric sensitivity tails off gradually at lower frequencies, and the sensitivity curve can be followed out to a frequency which depends primarily on the sensitivity of the detecting apparatus. The question then arises whether the shape of these curves, especially near the threshold, cannot be simply accounted for in terms of the temperature effect on the electron distribution in the metal. The observed curves bear obvious characteristics suggesting this origin rather than any change in work function with temperature. It is of course necessary, however, to examine possible temperature effects which may arise from the form of



the boundary transmission coefficient D(W), or from the form of the absorption coefficient of electrons of given energy for light of given frequency, so far as these functions are known. Probably it is more correct to fuse them together and regard their combined effect as a transition probability that under the action of light of unit intensity and frequency ν an electron originally in a given stationary state in the metal shall become a photo-electron with energy greater by $h\nu$. It may be stated at once that the observed results for silver, gold, tin,⁶ potassium (one temperature),⁷ and tantalum appear to be completely accounted for by the change of distribution of the electrons with the temperature. The excellent agreement between the forms of the observed and

- ⁶ Goetz, Phys. Rev., 33, 373 (1929).
- ⁷ Lawrence and Linford, Phys. Rev. 36, 482 (1930).

theoretical curves allows the use of a convenient graphical method for determining the true threshold from the general form of the whole family of sensitivity curves, which is thus of considerably greater certainty than any obvious method of extrapolating the observed curves to zero photoelectric current. At the same time, the whole effect here examined makes a precise determination of threshold almost impossible without a really exhaustive and reliable theory of the photoelectric effect.

Though any attempt to reinvestigate in detail the theory of the photoelectric effect would obviously be out of place in this paper, it is necessary to consider what corrections to this simple calculation are likely to be required by a more complete theory. We are interested here only in the form of the sensitivity curves in the immediate neighborhood of the threshold, and therefore factors like powers of ν in the transition probability can all be omitted, though they are of course of first class importance for a more general study of the whole sensitivity curve. It is only factors like $(\nu - \nu_0)^s$ where ν_0 is the threshold frequency which really matter to us. There are at present two not entirely consistent theories which we shall describe more closely later. According to one of these, the transition probability introduces no important factor and leaves unaltered the elementary theory of the form of the sensitivity curve near the threshold. According to the other, there is an extra factor introduced, of the form $(\nu - \nu_0)^{-1/2}$, which slightly modifies the shape and the temperature dependence. We therefore analyse the observations here according to both theories. The variation in the curves and their temperature dependence is about the limit of what the observations will stand. Excellent fitting is obtained on both theories, but that obtained with the simplest theory is slightly the better. Observations over a wider temperature range would probably allow one to discriminate between the theories.

In Figs. 1 and 2 we have shown curves for silver, gold, and tantalum because the tantalum sensitivity curves, in addition to behavior near the threshold similar to the curves for silver, show a new feature—a temperature-dependent general slope as they straighten out, instead of an asymptotic coalescence. There are symptoms of the same effect, but much less marked, for gold. Possible explanations of this are mentioned below, but they seem hardlysatisfactory, and at present it is wisest to record this feature as not yet explained. It is important to see if it can be correlated with any special feature in the thermionic emission formula and this experiment will be undertaken by Dr. Cardwell.

The precise hypothesis which succeeds so well in correlating the observed effect near the threshold is that the photoelectric sensitivity or number of electrons emitted per quantum of light absorbed is to a first approximation proportional to the number of electrons per unit volume of the metal whose kinetic energy normal to the surface augmented by hv is sufficient to overcome the potential step at the surface. We may call this number the number of available electrons. As we have said, this number as a function of v and T near the threshold is left unaltered by one of the two current theories.

Before these results were finally written up, I became acquainted with a

paper by Lawrence and Linford⁷ on the effect of strong electric fields on the photoelectric threshold (the Schottky lowering of the work function), in which they point out incidentally that the form of their curves (at room temperature only) near the threshold can be satisfactorily accounted for by the same assumption. The results here recorded are in entire agreement with theirs, but since this discussion is concerned with the analysis of somewhat elaborate data at many temperatures specially obtained for this purpose, it appears desirable to present them in full, with this acknowledgment of anticipation.

§2. The Number of Available Electrons

In a gas of electrons obeying the Fermi-Dirac statistics the number of electrons per unit volume having velocity components in the ranges u, u+du, v, v+dv, and w, w+dw (u normal to the surface) is given by the well-known formula

$$n(u, v, w) du dv dw = 2 \left(\frac{m}{h}\right)^3 \frac{du dv dw}{e^{\left(\frac{1}{2}m(u^2 + v^2 + w^2) - \epsilon^*\right)/kT} + 1}$$
(1)

where ϵ^* is to be adjusted so that the total number of electrons per unit volume has the correct value. To a first approximation ϵ^* is constant and equal to the energy of the electron level of highest energy which is filled at the absolute zero. This approximation is to be expected to be a good one over a wide range of temperature.⁸ The number per unit volume $\bar{n}(u)du$ with velocity component normal to the surface in the range u, u+du is given by

$$\bar{n}(u)du = 2\left(\frac{m}{h}\right)^{3} du \int_{0}^{\infty} \int_{0}^{2\pi} \frac{\rho d\rho d\theta}{e^{\frac{1}{2}m(u^{2}+\rho^{2})-\epsilon^{*}/kT}+1},$$
$$= \frac{4\pi kT}{m} \left(\frac{m}{h}\right)^{3} \log\left\{1 + e^{(\epsilon^{*}-\frac{1}{2}mu^{2})/kT}\right\} du.$$
(2)

We shall denote the total height of the potential step at the boundary by χ_0 and write $\chi = \chi_0 - \epsilon^*$, so that to the usual approximation χ is the thermionic work function.

We first experimented with the hypothesis that the number of available electrons was the number with sufficient *total* energy to escape, after the addition $h\nu$ to the usual energy. We may call this number N_A . Then obviously

$$N_{A} = 8\pi \left(\frac{m}{h}\right)^{3} \int_{\frac{1}{2}m\rho^{2}=\chi_{0}-h\nu}^{\infty} \frac{\rho^{2}d\rho}{e^{(\frac{1}{2}m\rho^{2}-\epsilon^{*})/kT}+1}$$

= $4\pi \left(\frac{m}{h}\right)^{3} \left(\frac{2 k T}{m}\right)^{3/2} \int_{0}^{\infty} \frac{\{y + (\chi_{0} - h\nu)/kT\}^{1/2}}{e^{y + (\chi h\nu)/kT}+1} dy.$

This expression can be simplified without spoiling its adequacy. For since we are concerned with values of $h\nu$ near the threshold $(h\nu \neq \chi)$, $h\nu - \chi$ is comparable with kT, while $\chi_0 - h\nu$ is always large. It is therefore a sufficiently good

⁸ Fowler, Statistical Mechanics, pp. 541-599 (Cambridge, 1929).

approximation to neglect y in $\{y+(\chi_0-h\nu)/kT\}^{1/2}$; the error in so doing can easily be investigated exactly if desired. Thus

$$N_{A} = \frac{4\pi (2mkT)^{3/2}}{h^{3}} \left(\frac{\chi_{0} - h\nu}{kT}\right)^{1/2} \int_{0}^{\infty} \frac{dy}{e^{y + (\chi - h\nu)/kT} + 1},$$

$$= \frac{4\pi (2m)^{3/2}}{h^{3}} kT (\chi_{0} - h\nu)^{1/2} \log \left\{1 + e^{(h\nu - \chi)/kT}\right\}.$$
(3)

As $T \rightarrow 0$ this reduces to the form

$$N_A \propto (\chi_0 - h\nu)^{1/2} (h\nu - \chi) \qquad (h\nu > \chi),$$
 (4)

$$= 0 \qquad (h\nu < \chi). \qquad (4')$$

At the threshold $h\nu = \chi$, $N_A \propto T$.

While such a formula for the number of available electrons presents some of the characteristic features of the curves of Figs. 1, 2, it is at once evident that it is not of the correct form. The observed variation with T near the threshold is clearly faster than that predicted, and still more, no reasonable extrapolation of the observed curves to zero temperature can be adapted to (4), which is practically a straight line cutting the axis of zero sensitivity at a finite angle. More detailed examination soon proved conclusively that the whole predicted form was wrong. We therefore passed on to the examination of the hypothesis described in §1, which is of course more reasonable *a priori* and which has proved completely successful.

On this hypothesis the number of available electrons N_B will obviously be given by the formula

$$N_B = \int_{\frac{1}{2}mu^2 = \chi_0 - h\nu}^{\infty} \bar{n}(u) du$$

= $\frac{2\pi kT}{m} \left(\frac{2kT}{m}\right)^{1/2} \left(\frac{m}{h}\right)^3 \int_0^{\infty} \frac{\log \left\{1 + e^{-y + (h\nu - \chi)/kT}\right\}}{\left\{y + (\chi_0 - h\nu)/kT\right\}^{1/2}} dy$.

Just as before we can approximate to this, and obtain with sufficient accuracy

$$N_B = \frac{2\sqrt{2}\pi m^{3/2}}{h^3} \frac{k^2 T^2}{(\chi_0 - h\nu)^{1/2}} \int_0^\infty \log\left\{1 + e^{-y + (h\nu - \chi)/kT}\right\} dy.$$
(5)

This integral cannot be evaluated in finite terms except when $h\nu = \chi$, but we may obtain convenient expansions for it from which its values can be rapidly computed,

(i) When $(h\nu - \chi)/kT = \mu \le 0$ the logarithm may be expanded and integrated term by term. Then

$$N_{B} = \frac{2\sqrt{2}\pi m^{3/2}}{h^{3}} \frac{k^{2}T^{2}}{(\chi_{0} - h\nu)^{1/2}} \bigg[e^{\mu} - \frac{e^{2\mu}}{2^{2}} + \frac{e^{3\mu}}{3^{2}} - \cdots \bigg] \qquad (\mu \leq 0).$$
(6)

(ii) When $(h\nu - \chi)/kT = \mu \ge 0$

$$\int_{0}^{\infty} \log (1 + e^{-y+\mu}) dy = \int_{0}^{\mu} \log (1 + e^{-y+\mu}) dy + \int_{0}^{\infty} \log (1 + e^{-y'}) dy',$$
$$= \frac{\pi^{2}}{12} + \frac{1}{2} \mu^{2} + \int_{0}^{\mu} \log (1 + e^{-y''}) dy''.$$

The logarithm may be expanded and integrated term by term giving

$$\int_0^\infty \log (1 + e^{-y+\mu}) dy = \frac{\pi^2}{6} + \frac{1}{2} \mu^2 - \left[e^{-\mu} - \frac{e^{-2\mu}}{2^2} + \frac{e^{-3\mu}}{3^2} - \cdots \right].$$

Thus

$$N_B = \frac{2\sqrt{2\pi m^{3/2}}}{h^3} \frac{k^2 T^2}{(\chi_0 - h\nu)^{1/2}} \bigg[\frac{\pi^2}{6} + \frac{1}{2} \mu^2 - \bigg\{ e^{-\mu} - \frac{e^{-2\mu}}{2^2} + \frac{e^{-3\mu}}{3^2} - \cdots \bigg\} \bigg]$$

($\mu \equiv 0$). (6')

When $T \rightarrow 0$

$$N_B \propto \frac{(h\nu - \chi)^2}{(\chi_0 - h\nu)^{1/2}} \qquad (h\nu > \chi) \\ = 0 \qquad (h\nu < \chi) \end{cases}.$$
(7)

When $h\nu = \chi$, $N_B \propto T^2$.

The analysis of the observations described in the next section will be made on the assumption that the photoelectric current I per quantum of light absorbed is proportional to N_B .

§3. First Analysis of the Observations

It will be observed at once that if $I \propto N_B$ and N_B is given by (6) and (6') then

$$\frac{I(\chi_0 - h\nu)^{1/2}}{T^2} = Af(\mu) = Af\left(\frac{h\nu - \chi}{kT}\right),$$
(8)

where A is an unknown constant independent of ν and T and

$$f(\mu) = e^{\mu} - \frac{e^{2\mu}}{2^2} + \frac{e^{2\mu}}{3^2} - \cdots \qquad (\mu \le 0)$$

= $\frac{\pi^2}{6} + \frac{1}{2}\mu^2 - \left[e^{-\mu} - \frac{e^{-2\mu}}{2^2} + \frac{e^{-3\mu}}{3^2} - \cdots\right] \qquad (\mu \ge 0)$ (9)

Further, when $h\nu = \chi$ approximately, then $\chi_0 - h\nu = \epsilon^*$ approximately and to a first approximation $(\chi_0 - h\nu)^{1/2}$ is constant. For example if ν changes 15% away from a threshold ν_0 corresponding to about 4 electron-volts, $\chi_0 - h\nu$ which is of the order of 10 volts will change by 6% and $(\chi_0 - h\nu)^{1/2}$ by 3% only. A sufficiently exact analysis can therefore be made as follows:—

Taking logarithms of (8), we have

$$\log \frac{I}{T^2} = B + \phi \left(\frac{h\nu - \chi}{kT}\right) \tag{10}$$

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B being independent of temperature and frequency. The theoretical curve $\phi(\mu)$ can be plotted as a function of μ . It is shown in Fig. 3. For each observed curve of photoelectric current we plot log (I/T^2) from the observed values against the variable $h\nu/kT$, the scales of the logarithms and of $h\nu/kT$ or μ being the same. By adjustment of origin we then bring the observed curve of log (I/T^2) into coincidence with the theoretical curve of $\phi(\mu)$. But in doing so all the curves for one metal for different temperatures should normally fit the theoretical curve for the same shift of logarithmic origin, so long that is as B does not depend on T. The actual value of this shift is of no importance, but the $h\nu/kT$ shift gives the threshold ν_0 or χ/h since $h\nu_0/kT$ is the scale



point on the observed curve coinciding with $\mu = 0$ on the theoretical curve. The values of ν_0 so determined should, if the theory were exact, be independent of the temperature. Fig. 3 shows the agreement obtained in this way for silver, gold and tantalum. In the case of tantalum, where the observations show that *B* must have changed with the temperature, the vertical shifts used were forced to differ by the amount required to take up the change in *B*. For the other curves equal vertical shifts were imposed for all temperatures for any one metal. The suspicion of crossing observed for gold could be removed by a negligible correction.

It will be seen at once that the general agreement so obtained is remarkably good. The points for all temperatures can be reduced to a single smooth curve except perhaps for one or two irregularities in tantalum. The thresholds determined from the horizontal shifts which should theoretically be independent of the temperature are given below.

-	A	g		
°K	hv ₀ /kT	λ₀, Α	χ , volts	
296 673 873	$ \begin{array}{r} 184.8 \\ 82.2 \\ 63.3 \end{array} $	2620 2590 2590	$\begin{array}{r} 4.71 \\ 4.76 \\ 4.75 \end{array}$	averages $\lambda_0 = 2600$ $\chi = 4.74$
· · ·	A	u		
°K	h_{ν_0}/kT	λ, Α	χ, volts	
296 733 1013	$ 191.0 \\ 78.0 \\ 56.5 $	2530 2500 2500	$ \begin{array}{r} 4.86 \\ 4.92 \\ 4.92 \\ 4.92 \end{array} $	averages $\lambda_0 = 2510$ $\chi = 4.90$
	Т	ìa		
°K	$h \nu_0 / k T$	λ₀, Α	χ , volts	
293 973	162.5 49.5	3010 2970	$\begin{array}{r} 4.10\\ 4.14\end{array}$	averages $\lambda_0 = 2990$ $\chi = 4.12$

Though the small variation in λ_0 goes in the same direction and is of about the same amount for all three metals, it is extremely doubtful if it is really significant.

The results for tin and potassium give equally good fits with the theoretical curve; Lawrence and Linford have already pointed this out for their potassium results. From Goetz's observations on tin the results are as follows.

Substance	°K	$h \nu_0 / k T$	λ_0, A	χ, volts	λ_0 . Goetz
β-tin γ-tin (1) liquid	358 483 673	$142.5 \\ 103.0 \\ 72.0$	2810 2880 2955	$\begin{array}{r} 4.39 \\ 4.28 \\ 4.17 \end{array}$	2740 2820 2925

(1) Observations rather irregular.

There is here a decided change of threshold with temperature, or rather presumably with crystalline form and on melting. It would be interesting to confirm this result with other meltable metals. The size and direction of the changes in χ compared with the variations for the other metals are such that we can be confident that the effect is real. The differences between our λ_0 and Goetz's are due to the use by him of an empirical method of extrapolating to zero current.

§4. Attempts at a More Exact Theory

A proper theory of the photoelectric effect must calculate quantum mechanically the chance that an electron in a definite state of motion inside the metal shall "pick up" a quantum $h\nu$ and appear in a new state of motion as a photoelectron. Such a theory was first attempted by Wentzel⁹ and his theory has been improved by Houston¹⁰ and by himself¹⁰; Its theoretical basis hardly appears to be entirely satisfactory in its original form. Apparently more satisfactory discussions have more recently been given by Fröhlich¹¹ and by Tamm and Schubin.¹² It does not appear even now that their interpretations of their theoretical formulae are entirely reliable, but the general principle of the calculation seems to be correct. This newer theory can be presented for our purposes in an elementary manner, a knowledge of which I owe to conversations with Professor Frenkel.

From an electron with kinetic energy $\frac{1}{2}mu^2$ normal to the surface, an escaping photoelectron can be created with energy normal to the surface $\frac{1}{2}mu^2 + hv$. The work of Fröhlich and of Tamm and Schubin seems to show that the problem can be discussed one-dimensionally, the other velocity components being without effect. We shall be content to assume this hardly obvious result for our elementary presentation. The probability of this event will be proportional to the intensity of the light, and the dominating factor in the calculation of any such probability is always

$$\left|\int \Psi_1^* V \Psi_0 d\omega\right|^2,$$

where the integration is over the configuration space of the electron, V is the perturbing electromagnetic potential of the light in operator form, and Ψ_0 , Ψ_1 are the properly normalized wave-functions for the electron in its initial and final states. Now Ψ_0 for the initial state is of the form

$$(ae^{2\pi i px/h} + a^* e^{-2\pi i px/h})e^{-2\pi i Wt/h}$$

inside the metal (constant potential energy), and dies away exponentially in the region where the potential energy exceeds the total energy. The *a* and a^* are adjusted to normalize Ψ_0 for one electron in the metal and do not depend on ν . On the other hand Ψ_1 representing one actually emerging electron must be normalized to represent an *emergent flux* of one electron and the external wave function is therefore of the form

$$\frac{1}{W'^{1/4}} e^{2\pi i (p'x - W'^{t})/h},$$

$$W' = \frac{1}{2}mu^{2} + h\nu - \chi_{0} > 0.$$
(11)

where

It appears that this $W'^{1/4}$ is the only factor with a sensitive dependence on ν . Over the small light frequency ranges in which we are here interested, factors such as powers of ν itself are of slight interest. One may therefore expect the probability of emergence to contain a factor

⁹ Wentzel, Probleme der Modernen Physik, Leipzig 1928 p. 79 Sommerfeld's Festschrift).

¹⁰ Quoted by Lawrence and Linford (loc. cit) from private communications.

¹¹ Fröhlich, Ann. d. Physik 7, 103 (1930).

¹² Tamm and Schubin, Zeits. f. Physik 68, 97 (1931).

$$\frac{1}{(\frac{1}{2}mu^2 + h\nu - \chi_0)^{1/2}}$$

and no other factors of great importance. A detailed investigation confirms this.

On referring to (2) we now see that, provided nothing else has been overlooked, the photoelectric current should be proportional near the threshold to

$$\frac{4\pi kT}{m} \left(\frac{m}{h}\right)^3 \int_{\frac{1}{2}mu^2 \chi_{0-h\nu}}^{\infty} \frac{du}{(\frac{1}{2}mu^2 + h\nu - \chi_0)^{1/2}} \log \left\{1 + e^{(\epsilon^* - \frac{1}{2}mu^2)/kT}\right\},$$

which can be reduced, omitting constants of proportionality to

$$P = \frac{T^{3/2}}{(\chi_0 - h\nu)^{1/2}} \int_0^\infty \frac{dy}{\sqrt{y}} \log (1 + e^{\mu - y}), \qquad (12)$$

where as before

$$\mu = \frac{h\nu - \chi}{kT} \cdot$$

According to (12) therefore, we shall have a photoelectric current which as $T \rightarrow 0$ takes the form

$$P \propto \frac{(h\nu - \chi)^{3/2}}{(\chi_0 - h\nu)^{1/2}} \qquad (h\nu > \chi),$$
(13)

When $h\nu = \chi$, $P \propto T^{3/2}$. These forms are not a priori impossible. Equation (13) agrees with equation (6'') of Tamm and Schubin to the approximation to which we are working here. To analyse the experiments we have to plot

$$\log\left\{I\frac{(\chi_0 - h\nu)^{1/2}}{T^{3/2}}\right\}$$

against $h\nu/kT$ and compare it with the theoretical curve log $f(\mu)$ where

$$f(\mu) = \int_0^\infty \frac{dy}{\sqrt{y}} \log (1 + e^{\mu - y}) dy.$$
 (14)

When $\mu \leq 0$

$$f(\mu) = \sqrt{\pi} \sum_{n=1}^{\infty} \frac{(-1)^{n-1}}{n} e^{n\mu}.$$
 (15)

When $\mu > 0$ there is no simple expansion available but there is the asymptotic expansion good for $\mu \ge 7$ or thereabouts.

$$f(\mu) \sim \frac{4}{3} \mu^{3/2} + \frac{\pi^2}{6} \frac{1}{\mu^{1/2}} + \frac{2}{\mu^{5/2}} \frac{1 \cdot 3}{2^2} \sum_{n=1}^{\infty} \frac{(-1)^{n-1}}{n^4} + \frac{2}{\mu^{9/2}} \frac{1 \cdot 3 \cdot 5 \cdot 7}{2^4} \sum_{n=1}^{\infty} \frac{(-1)^{n-1}}{n^6} + \cdots$$
(16)

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On the other hand the corrected results of Wentzel and Houston quoted above give no additional factor sensitive to ν and therefore yield sensitivity curves near the threshold essentially in agreement with the N_B of Eq. (7). Their revised theories have however, so far as I am aware, not yet been published. We shall analyse the experimental results again according to the formulae of this section without further theoretical discussion.

§5. Second Analysis of the Observations

The method of analysis is the same as that of §3. The results for silver, gold and tantalum are shown in Fig. 4. It is perhaps just possible to decide, on inspecting fairly large scale plots, that the fit is less good than the fit obtained in §3. The fit obtainable for tin and potassium is distinctly less good than the fit obtainable according to §3 but of course these data are not so suitable for accurate discussion. The threshold values are given below.

Ao

		-		
°K	$h\nu_0/kT$	λ_0, A°	χ , volts	
296 673 873	186.7 82.9 63.8	$\begin{array}{r} 259_{5} \\ 2570 \\ 2570 \\ 2570 \end{array}$	$4.75 \\ 4.79 \\ 4.79 \\ 4.79$	averages $\lambda_0 = 2580$ $\chi = 4.78$
	1	Au		
°K	$h\nu_0/kT$	λ_0, A°	χ , volts	
296 733 1013	192.2 78.5 56.7	$2520 \\ 248_{5} \\ 2490$	$\begin{array}{r} 4.89 \\ 4.95 \\ 4.94 \end{array}$	averages $\lambda_0 = 2500$ $\chi = 4.93$
		Га		
°K	$h\nu_0/kT$	λ_0, A°	χ , volts	
293 973	163.8 50.0	298 ₅ 2950	4.13 4.18	averages $\lambda_0 = 2970$ $\chi = 4.16_5$

As with the results of §3 there is little or no significant variation to be detected here. The different methods of extrapolating to zero temperature (as it were) give values of λ_0 differing by about 20 A° and values of χ differing by about 0.04 volts. Until we can decide which theory must be preferred, there must remain this amount of uncertainty in the determination of the threshold.

§6.

The change of slope which leads to the intersection of the sensitivity curves for tantalum and perhaps for gold has yet to be considered. It is a change of about 20% for tantalum, and it is tempting to try to correlate it with the factor $(\chi_0 - h\nu)^{-1/2}$ which occurs in both theories for the sensitivity. This factor is essentially $(\epsilon^*)^{-1/2}$ and to interpret the change of slope in this way without change of χ we should have to suppose that ϵ^* and χ_0 both increase equally with the temperature¹³ by about 40%. This is most unlikely! It remains to be seen whether a more exact theory will give other factors of

this type, so that the effect could be accounted for by a smaller and more reasonable change. On the experimental side, it is desirable to know not only



whether this change correlates with some peculiarity in the thermionic emission, but also whether the more normal behaviour is that of silver with no such effect, or gold with a very small one.

§7. CONCLUSION

In conclusion it seems fair to maintain that the temperature effect observed in the photoelectric sensitivity of all three metals (except for the change of slope for tantalum) is a result of the temperature effect on the distribution of the electrons among their various levels in the metal and that no other primary changes are taking place at these temperatures. We may also be confident that further study of the effect especially (if possible) over a wider temperature range and in connection with the thermionic emission will help to throw considerable light on the theory of metals.

It is a pleasure to thank Professor Mendenhall for the opportunity to become acquainted with the experimental work on this subject, afforded by a temporary post in his department, and Messrs. Winch and Morris for their generous assistance in the analysis of the experimental material, both their own, and of other observers.

¹³ In view of the definition of ϵ^* this must be interpreted to mean that some change takes place, e.g., an increase in the number of free electrons such that if the new state were extrapolated back to zero temperature we should require a larger value of ϵ^* .