On the Influence of Temperature upon the

Photo-electric Effect

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A

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Summary.

1. Interpretation of the threshold frequency.

A discussion is given of the conclusion, reached by Millikan, that in the photo-electric effect the energy of the light is transferred to the free electrons of the metal as well as to the bound electrons, and the threshold frequency $\nu_0$ is interpreted by the equation $h\nu_0 = \phi_p - E_k$ , where $\phi_p$ is the work necessary to remove a free electron from the metal, and $E_k$ the average kinetic energy of a free electron in the metal. In cases where $E_k$ is not small compared with $\phi_p$ the theory leads to a lack of sharpness in the definition of $\nu_0$. The observed uniformity of stopping potentials is due, according to the theory, to the smallness of the Peltier effect.

2. Temperature variation of the long wave-length limit.

From Millikan's free electron theory and Richardson's thermodynamical theory of electron emission the following expression is derived for the variation of the long wave-length limit with temperature: $\frac{\partial \lambda_0}{\partial T} = \frac{\lambda_0^2}{hc} e \sigma$ , $\sigma$ being the Thomson coefficient. In most cases $\lambda_0$ should be practically independent of temperature.

3. Effect of prolonged heating on the photo-electric current from aluminum for 2537 A.

A solid target was heated in vacuum by high frequency induction for many hours to near the melting point, but the photo-electric current remained strong.

4. Variation with temperature of the photo-electric current from aluminum for 2537 A.

After prolonged heating, the current was found to remain constant within 1/2 per cent as the target cooled from 400 to 100 C. This constancy is interpreted as fairly conclusive evidence that the shift of the long wave-length limit with change of temperature is less than 1 A. The limit was found to be at about 2700 A.

Similar observations with a nickel target and 2412 A gave inconclusive results as in spite of heating to 1300 C and reduction of the oxide on the surface by heating in hydrogen, reproducible results were not obtained.

Introduction.

The influence of temperature upon the photo-electric effect has been studied by a number of investigators[1], all with negative results. The photo-effect was found independent of temperature within the experimental errors. In the earlier investigations monochromatic light was not used, and the errors of observation were large. Kopplus recently determined the long wave-length limit of platinum, and found it independent of temperature to less than 1 A for the range $50°$ to $500°$C. Other experiments[2], however, have shown that the apparent long wave-length limit of platinum is gradually decreased as the surface is being denuded of occluded gases by prolonged heating at higher and higher temperatures. The question as to whether or not the photo-electric sensitivity is an intrinsic and invariable property of metals has thus been raised again.

In the present investigation the variation of the long wave-length limit to be expected from a theoretical standpoint is discussed, and an attempt has been made to determine the temperature variation upon surfaces freed from gases as well as possible by heating in vacuum.

### 1. Interpretation of the long wave-length limit.

In 1921 Millikan[3] found that the "stopping potential", i.e. the potential that must be applied in order to prevent the photo-electrons from reaching the receiver, is quite accurately the same for different emitting metals, provided the same receiver is used. From earlier experiments by Hermann[4] a similar inference may be drawn. This peculiar fact led Millikan to the conclusion that <u>the electrons which escape from a metal with the maximum velocity under the influence of light are the free electrons of the metal</u>. On account of the great importance of this result for the interpretation of the photo-electric phenomena a brief discussion of it will be given. It will be shown that it furnishes an interpretation of the long wave-length limit and leads to definite conclusions as to the temperature variation.

It is immaterial for the analysis here given whether we assume that the light energy is transferred <u>directly</u> to the free electrons of the metal or indirectly, as suggested by Epstein, through collisions of the second kind. Millikan's conclusion is that the light energy $h\nu$ is transferred undiminished to electrons which are in the same state as those emitted as thermo-electrons. Very little is known about the conditions of the free electrons. We shall, therefore, make no special assumptions but use only two equations,

derived by O. W. Richardson[5] from purely thermodynamical
though not quite rigorous considerations. These equations
are

$$\frac{\partial \phi}{\partial T} = \frac{3}{2} k - e \sigma \qquad (1)$$

$$\phi' - \phi'' = e V - e T \frac{\partial V}{\partial T} \qquad (2)$$

where $\phi$ is the increase of energy which accompanies the
transference of an electron from the interior of a metal
to a point outside, $\phi'$ and $\phi''$ being the values for two differ-
ent metals; T denotes the absolute temperature, k Boltzmann's
constant, e the charge of an electron, $\sigma$ the coefficient
of the Thomson effect, and V the contact difference of pot-
ential between the two metals. The term $eT\frac{\partial V}{\partial T}$ may also be
written eP, P being the Peltier coefficient. The terms $e\sigma$
and $eT\frac{\partial V}{\partial T}$ are, in general, small compared with the other terms
in the equations. As Bohr[6] has pointed out, P and $\sigma$ are
not identical with the coefficients found by experiments,
but this fact is of little importance for the present
considerations.

The values found for the specific heats of metals
and for the Thomson coefficients indicate that the average
kinetic energy of the free electrons within the metal is, in
general, much smaller than the equipartition value 3/2 kT.
We will, therefore, disregard the fact that the kinetic
energy is not the same for all the free electrons. We will

denote by $E_p$ the potential energy of a free electron, and by $E_k$ its average kinetic energy within the metal, and will place $\phi = \phi_p + \phi_k$, where $\phi_p$ is the gain in potential energy, and $\phi_k$ the gain in kinetic energy accompanying the transference of a free electron from the metal to the surrounding electron atmosphere. If the heat energy of the electron atmosphere be assumed to equal that of a moatomic gas, we have

$$\phi_k = 3/2 \ kT - E_k .$$

We are now prepared to give an interpretation of the term $h\nu_0$ in the expression for the maximum kinetic energy of the photo-electrons, which was predicted by Einstein and verified by Millikan, viz.

$$(V_S - V_F)e = h\nu - h\nu_0 , \qquad (3)$$

where $V_S$ denotes the stopping potential, and $V_F$ the contact difference of potential between emittor and receiver. If, following Einstein, we assume that the energy $h\nu$ of a light quantum is transformed to kinetic energy of a single electron, then the largest possible value of the kinetic energy of a photo-electron escaping from the metal must be $E_k + h\nu - \phi_p$. The frequency $\nu_0$ for which this is zero is the threshold frequency, and we have

$$h\nu_0 = \phi_p - E_k . \qquad (4)$$

Instead of using this expression for $h\nu_0$ Millikan[3], placing $h\nu_0 = \phi$, used a value which is $3/2 \ kT$ larger. This, however, did not influence his result because the value of

h$\nu_o$ for one metal was subtracted from that for another.

Substituting for h$\nu_o$ in (3), and subtracting the equations for two different metals, we get

$$-(V_s' - V_s'')e + Ve = \phi_p' - \phi_p'' - E_k' + E_k'',$$

where $V = V_F'' - V_F'$ is the contact difference of potential between the two metals. Now substituting the value for Ve obtained from (2), and remembering that $\phi_k + E_k = 3/2$ kT, we simplify the equation to

$$-(V_s' - V_s'') + T\frac{\partial V}{\partial T} = 0, \qquad (5)$$

The last term in (5), from the values of the measured Peltier coefficients, is of the order of magnitude of $10^{-3}$ to $10^{-2}$ volts. Millikan's conclusion that the light energy is transferred to the free electrons of the metal leads, therefore, to a simple explanation of the independence of the stopping potential upon the nature of the emittor. From (5), however, it will be seen that <u>accurate measurements of stopping potentials should reveal slight differences approximately equal to the Peltier coefficients, expressed in volts</u>. It would be of great importance for the theory if determinations of stopping potentials could be made so accurately as to allow a test of (5).

The expression (4) for h$\nu_s$ is valid only when the differences in the kinetic energies of the free electrons may be disregarded. It will, therefore, not hold at high temperatures. Under such conditions, according to the free

electron theory, an appreciable lack of sharpness in the definition of the threshold frequency and the stopping potential should occur.

It seems impossible to explain the equality of stopping potentials for different metals by any other simple theory of the photo-electric effect. The assumption that the light energy is transferred to electrons bound in the atoms would imply, as shown by reasoning similar to that given above, that the electrons bound in atoms of different metals possess the same energy. This is at variance with all we know about atomic structure. The assumption that the uniformity of stopping potentials is due to a uniform gas layer on all metals would lead also to a uniform threshold wave-length and to a uniform photo-electric sensitiveness, due corrections being made for differences in reflecting power. This is not in accord with observations.

The hypothesis that light energy can be transferred entirely to a free electron may seem rather strange at a first glance. It may, therefore, be worth while to note that it may be arrived at by a natural generalization of the ideas by which the continuous absorption spectrum of hydrogen or sodium is explained. It is assumed that when light of shorter wave-length than the limit of the absorption series is absorbed, the electron is knocked out with a kinetic energy equal to the difference between $h\nu$ and the work necessary for ionization. But if this absorption process may take place however

loosely the electron be bound, it should also occur in the limiting case of the electron being free.

2. Temperature variation of the long wave-length limit.

The influence of a change in temperature upon the threshold frequency $\nu_0$ may be found immediately from the theory discussed above. Since $\phi = \phi_h + 3/2\ kT - E_k$, the equation (1) may be written

$$\frac{\partial}{\partial T}\left(\phi_h - E_k\right) = -e\sigma$$

but $\phi_h - E_k = h\nu_0$, hence

$$\frac{\partial(h\nu_0)}{\partial T} = -e\sigma \tag{6}$$

or

$$\frac{\partial\lambda_0}{\partial T} = \frac{\lambda_0^2}{hc}e\sigma , \tag{6 a}$$

$\frac{c}{\nu_0} = \lambda_0$ being the long wave-length limit.

The temperature variation of the threshold frequency or the long wave-length limit is thus proportional to the Thomson coefficient. Since the Thomson effect is always very small, the long wave-length limit should be practically independent of temperature. For aluminum Borelius and Gunneson[7] have found $\sigma = -0.56$ microvolts per degree at $400^\circ$K, while $\lambda_0 = 2700$ A. Substituting these values we get $\frac{\partial\lambda_0}{\partial T} = 3.3 \times 10^{-4}$ A per degree, i.e. a shift in long wave-length limit of 1/10 A for a change in temperature of 300 degrees. For all the metals for which both $\sigma$ and $\lambda_0$ are measured (6 a) gives so small values for the temperature variation that,

with the accuracy with which photo-electric measurements
are now being carried out, it should not be possible to
detect the variation. For the alkali metals, however, a
measurable variation may be expected since $G$ is large, as
indicated by the values found for the specific heats, and
since $\lambda_o$ is also large.

In the preceding only the long wave-length limit
has been considered. No satisfactory theory has yet been
given for the velocity distribution nor for the magnitude
of the photo-electric saturation current. The reason for this
is partly the lack of a satisfactory substitute for the old
electron theory of metals and partly the lack of reliable
photo-electric data. We shall, therefore, not attempt to
treat theoretically the effect of temperature upon the photo-
electric current.

### 3. Experimental method and apparatus.

A variation of the long wave-length limit has been
searched for by observing the photo-electric saturation
current at different temperatures of the emitting metal,
using a wave-length just below the long wave-length limit.
Actual measurements would require observations with differ-
ent wave-lengths. If photo-currents are found to be constant,
it may be reasonably inferred that the long wave-length
limit is independent of temperature.

Photo-electric targets of aluminum and nickel were
heated in vacuum by high frequency induction. Two Western
Electric 212-A tubes, in parallel, served as generators of
the high frequency currents which were sent through the
primary coil of thick copper tubing surrounding the photo-
electric tube. The targets were solid cylinders of diameter
1.9 cm and length 2.0 or 1.2 cm. During the slow cooling of
the target the saturation current was measured by the aid
of a quadrant electrometer connected to the cylindrical
receiver which partly enclosed the target.

Fig. 1 shows the two types of photo-electric tubes
used. Both were made of Pyrex glass. A quartz window was
cemented on with a high temperature cement. The temperature
of the seal was kept below $100^{o}C$ by water cooling. In tube
A, with which most of the experiments with aluminum were
made, the target was fixed with respect to the receiver.
When the target was heated the receiver would also be heated.
In order to prevent the receiver, which was made of copper,
from melting the heating of the target had to be applied
intermittently, so as to let the thin copper cylinder cool
for a short time between consecutive heatings. In tube B,
which was used for nickel, the target was heated outside the
receiver, which was also made of nickel, and then lifted up
into the receiver by a simple magnetic device. The light
reached the target through a slit in the top of the receiver.
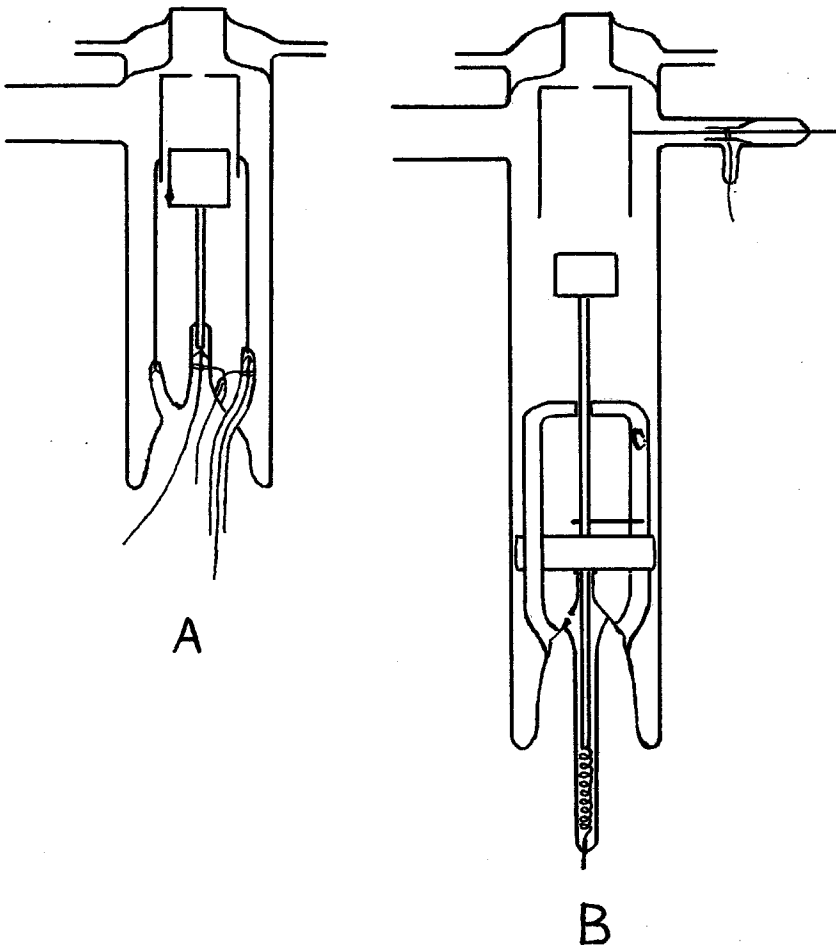Both tubes had, to begin with, thermo-couples for measuring

A

B

F I G 1

the temperature of the target. These, however, soon got out of order. In one case the junction moved out of the target at the first heating to the melting point; in another case a discharge took place from the coil outside the tube to the thermo-couple wire inside. Enough data were obtained, however, to permit an estimate of the temperature during the cooling. The only temperature used for the calibration of the thermo-couples was the melting point of aluminum.

The tubes could not be used very long or the glass would be heated to the softening point by radiation from the target and by currents in the layer of metal deposited on the glass wall by evaporation of the target.

A 220 volts quartz mercury lamp and a Hilger monochromatic illuminator were used for illumination. The lamp was enclosed in an asbestos box and run at a constant high-voltage, the voltage drop in the arc alone being about 120 volts. By means of a large quartz lens an image of the arc, of nearly natural size, was formed on one slit of the illuminator and adjusted so that the middle coverdd the slit. The light then just filled the collimator lens. Under these circumstances the variations in the intensity of the illumination were found to be practically negligible. The photoelectric tube was set up vertically so that the quartz window was only a few mm from the other slit of the illuminator, the slit in the receiver being large enough to let the

slightly divergent light to pass to the target. The pressure in the tube was in most cases so low that no reading could be obtained by a McLeod gauge even when the target was heated.

4. The cleaning up of the aluminum surface by heating.

With aluminum the photo-currents were so large that they could be measured by the constant deflection obtained when the two pairs of quadrants were shunted with a large resistance consisting of a line of ink on a strip of paper. The sensitiveness of the electrometer was about 1500 mm per volt at a scale distance of 1 m. In almost all the experiments with aluminum the line 2537 A was used.

Heating of the target was found to have a great effect upon the photo-electric current. When aluminum has been exposed to air, or when it has been kept for a long time in a vacuum without being heated, the photo-current is small. A short heating, however, will produce a considerable increase in the current; and as the heating is continued, and the temperature raised, the photo-current will reach a maximum, decrease, and then increase again until a value of 5 or 10 times the original is reached. Further heating to a temperature close enough to the melting point produces a decrease in the current. When the aluminum had been heated for a long time, and the melting point had been reached several times

during the intermittent heating, the photo-current had attained a value of about one third of the highest value observed, and continued heating produced no furhher change of the photo-current. In one case the following values of the current for 2537 A were obtained during the process of cleaning up, the target being heated several times between consecutive values:

6.4, 25.8, 24.0, 18.9, 20.8, 27.7, 43.0, 45.5, 18.5, 17.5.

The effect of the cleaning up by heating upon the photo-current from aluminum is of the same general character as that found for platinum by other observers[2]. The fact that the photo-current remains strong after prolonged heating at the melting point is an evidence against a fundamental dependence of the photo-effect upon surface impurities. Obviously, the heating has not produced a complete cleaning up of the aluminum surface. Close to the melting point, however, a breaking up of the surface occurs, so that it becomes granular. Whether the currents are due mostly to aluminum or to the oxide is unknown.

The following observations may be of interest in the difficult problem of determining the nature of the surface impurities. When the photo-current was observed for a sufficiently long time after the heating an increase in the current was always observed. However, if the liquid air were removed from the charcoal tube between the photo-electric tube and
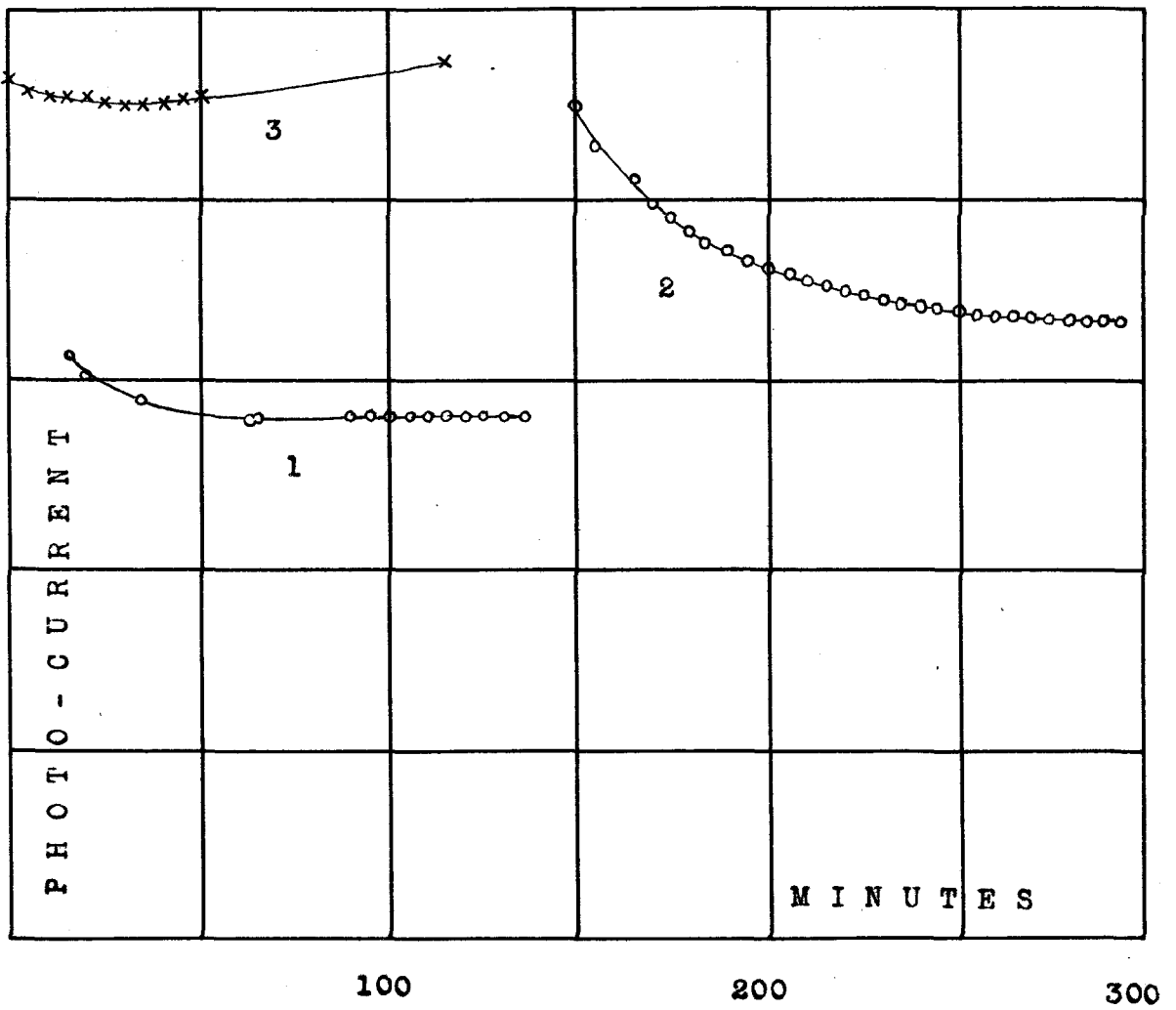
F I G  2

the pumps, leaving liquid air only on a trap closer to the
pumps, a considerable decrease in the current would immediate-
ly set in, amounting to about 30 per cent of the initial
value in two minutes and to 40 per cent in ten minutes.

### 5. Temperature variation with aluminum.

As long as the aluminum was not sufficiently cleaned
up by heating a considerable variation of the photo-electric
current was observed during the cooling. In all cases the
photo-current was found to decrease at first. The current
would generally decrease and then become almost constant; in
some cases, however, an increase followed the decrease. A
typical example is given in Fig. 2 Curve 1, the photo-current
being plotted against time of cooling.The first readings were
taken two or three minutes after the thermionic current had
become negligible, the temperature then being about 400°C.
By the time the photo-current had become constant the temp-
erature was about 150°C. The constancy of the current during
the last part of the cooling is remarkable. This may be better
seen from Table I which gives all the readings taken during
twenty minutes. The smallness of the variations gives an idea
both of the constancy of the light intensity and of the
accuracy with which the photo-currents could be measured.

That the decrease observed in the beginning is not
due simply to a dependence of the photo-current upon tempera-

## Table I.

| Time | Photo-current (2537 A) | Time | Photo-current (2537 A) |
|------|------------------------|------|------------------------|
| 110 min | 28.20 (cm) | 120 min | 28.13 (cm) |
| 111 | 28.18 | 121 | 28.12 |
| 112 | 28.15 | 122 | 28.15 |
| 113 | 28.14 | 123 | 28.10 |
| 114 | 28.11 | 124 | 28.13 |
| 115 | 28.13 | 125 | 28.15 |
| 116 | 28.12 | 126 | 28.10 |
| 117 | 28.15 | 127 | 28.20 |
| 118 | 28.15 | 128 | 28.12 |
| 119 | 28.14 | 129 | 28.14 |

## Table II.

| Time | Photo-current (2537 A) |
|------|------------------------|
| 0 min | 17.2 (cm) |
| 10 | 17.3 |
| 20 | 17.35 |
| 30 | 17.29 |
| 40 | 17.30 |
| 50 | 17.33 |
| 62 | 17.6 |
| 70 | 17.8 |
| 80 | 18.0 |

ture is most clearly brought out by comparing Curve 1 with Curve 2, which was taken immediately after Curve 1, the target having been heated for three minutes to about 400°C between the two sets of readings.

The longer the aluminum was heated, and the higher the temperature to which it was heated, the smaller was the variation of the photo-current observed during the cooling. Curve 3 was obtained after the target had been kept red hot for 1 1/2 hour, the temperature never quite reaching the melting point. The total variation of the current is only about 3 per cent. However, in this case the aluminum was not yet cleaned up as much as possible.

Table II gives the result of the last experiment made with aluminum. The target had now been heated several hours daily for two months. It was very much deformed and displaced, and the next heating resulted in a break-down of the tube. Immediately before the readings were taken the target was heated for one hour, the temperature being kept close to the melting point which it reached several times. The electrometer zero was determined two minutes before and two minutes after every reading, and corrections were made for a slow motion of the zero amounting to 1.4 cm per hour. Almost no variation whatever of the photo-current is observed during the first 50 minutes of the cooling. The increase at lower temperatures indicates that some surface film is being

formed.

The experiments with aluminum have thus failed to detect any variation of photo-currents with temperature between 400°C and room temperature. In the temperature range 400°C to 100°C the photo-current obtained with 2537 A is found constant within 1/2 per cent.

From the constancy of the saturation current we may infer that the temperature variation of the threshold wave-length of aluminum is very small. An estimate of the change in long wave-length limit corresponding to a change in the current for 2537 A of 1/2 per cent may be obtained in the following way. The curve representing photo-current per unit intensity of illumination as a function of the wave-length will be nearly a straight line in the neighborhood of the long wave-length limit. If we assume that a small change in the limit simply produces a displacement of the curve parallel to the wave-length axis, then a constancy of the current within 1/2 per cent means a shift of the limit of less than 1 A, the limit being about 150 A from the wave-length used.

No accurate determination of the long wave-length limit was made. A rough determination gave for aluminum cleaned up by heating the limit 2700 A, which is much lower than that found by Richardson and Compton[8].

## 6. Experiments with nickel.

With nickel the results were not nearly as conclusive as with aluminum. The photo-currents were so small that the steady deflection method could not be used. The currents were measured by the rate of charging up of the receiver connected with one pair of quadrants. In order to clean up the target it was heated to 1300-1400° C. The tube could not stand a heating to this temperature for a very long time. Oxide on the surface was reduced by heating in hydrogen. The readings of the photo-current were started, as with aluminum, as soon as the thermionic current was negligible, which occurred at about 550° C.

A constant current was never obtained. Fig. 3 shows two of the curves obtained with 2412 A. Before Curve 1 was taken the target had been heated for 15 minutes at 1300-1400°C Curve 2 was obtained right after Curve 1, the target having been heated for 40 minutes between the two sets of readings. Though the current varies considerably during the cooling, the fact that there is no large variation during the first very rapid cooling indicates that the variation is not due simply to a dependence upon temperature of the photo-electric effect.

The long wave-length limit of nickel was roughly determined at 2500 A.

F I G 3
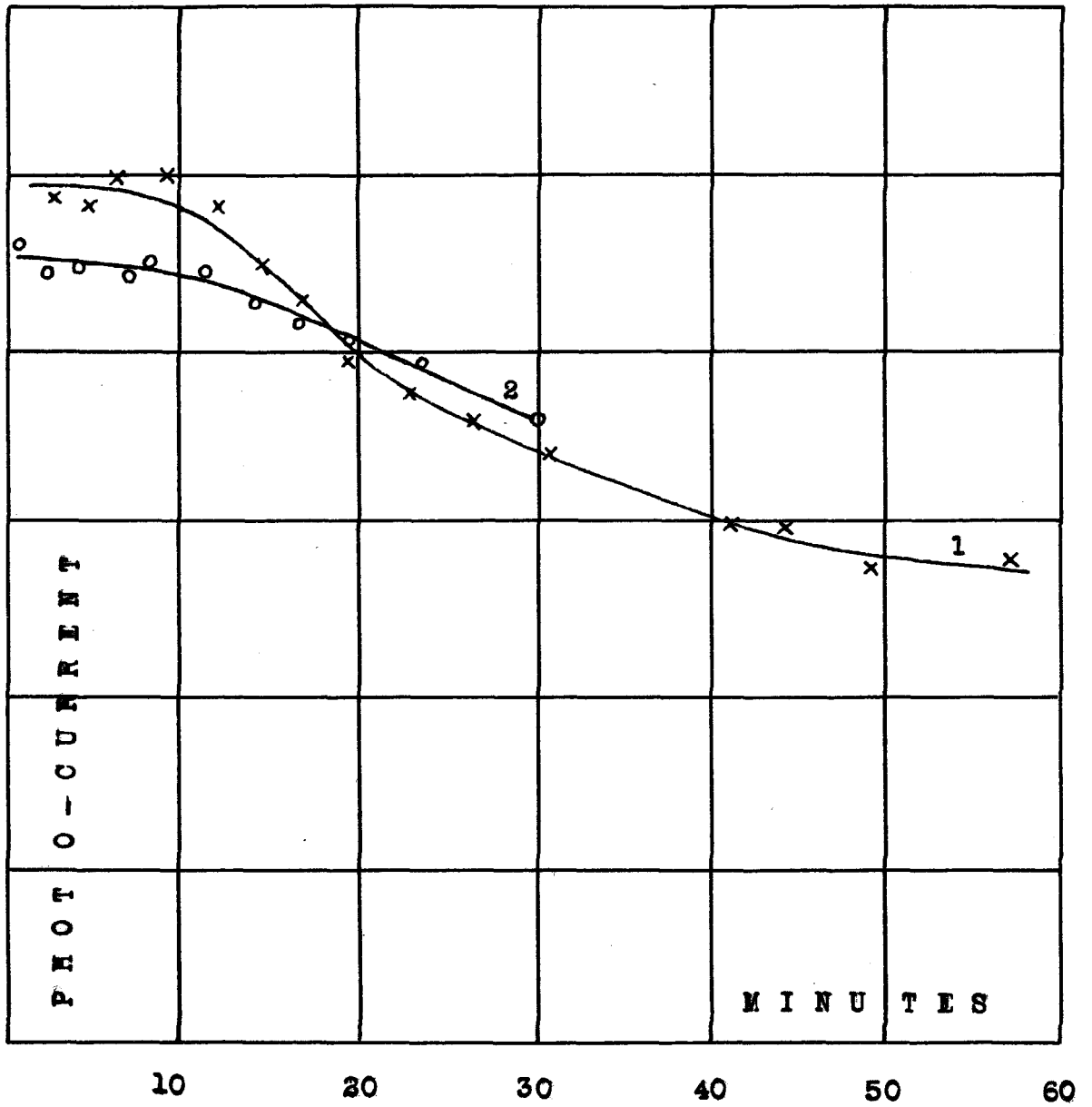
In conclusion, the writer wishes to express his great indebtedness to Professor R. A. Millikan who suggested the problem, and under whose direction the work was done.

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