ON THE INFLUENCE OF TEMPERATURE UPON THE PHOTO-ELECTRIC EFFECT

By J. Rud Nielsen*

ABSTRACT

Photo-electric threshold frequency for metals.—*Free electron theory.* A discussion is given of the suggestion by Millikan that in the photo-electric effect the energy of the light is transferred to the free electrons of the metals as well as to the bound electrons, and the threshold frequency ν_0 is interpreted by the equation $h\nu_0 = \varphi_p - E_k$ where φ_p is the work necessary to remove a free electron from the metal. In cases where E_k is not small compared with φ_p the theory leads to a lack of sharpness in the definition of ν_0. Neglecting variations of kinetic energy, the difference of stopping potentials comes out equal to the Peltier coefficient; hence the uniformity of stopping potentials for different metals observed by Millikan is due, according to the theory, to the smallness of the Peltier effect. *The variation of the long wave-length limit with temperature* comes out $\partial\lambda_0/\partial T = (\lambda_0^2/hc)e\sigma$, σ being the Thomson coefficient. In most cases λ_0 should be practically independent of temperature. *In the case of aluminum,* after prolonged heating, the photo-electric current due to $\lambda 2537$ was found to remain constant within 1/2 per cent as the target was cooled from 400° to 100°C and this constancy is interpreted as evidence that the shift of the long wave-length limit with change of temperature is less than 1A. The limit was found to be at about 2700A. Similar observations with a nickel target and 2412A 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.

Photo-electric current from aluminum for $\lambda 2537$.—(1) *Effect of prolonged heating* in vacuum by high frequency induction for many hours to near the melting point. The current remained strong. (2) *Effect of cooling from* 400° *to* 100°*C*. The current remained constant within 1/2 per cent.

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. Koppius[1] recently determined the long wave-length limit of platinum, and found it independent of temperature to less than 1A for the range 50° to 500°C. Other experi-

[1] Lienhop, Ann. der Phys. **21**, 281 (1906);
  Dember, Ann. der Phys. **20**, 379 (1906); **23**, 957 (1907);
  Ladenburg, Verh. d. Deutsch. Phys. Ges. **9**, 165 (1907);
  Millikan and Winchester, Phil. Mag. **24**, 188 (1907);
  Kunz, Phys. Rev. **29**, 174 (1909);
  Koppius, Phys. Rev. **18**, 443, (1921).

ments,[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] and Page[5] a similar inference may be drawn. This peculiar fact led Millikan to the conclusion that *the electrons which escape from a metal with the maximum velocity under the influence of light are the free, i.e. the conduction electrons of the metal.* 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 *directly* 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, which were derived by O. W. Richardson[6] from purely thermodynamical though not quite rigorous considerations. These equations are

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

$$\phi' - \phi'' = eV - eT \ \partial V/\partial T \tag{2}$$

[2] Hallwachs, Phys. Zeitschr. **21**, 561 (1920);
Sende and Simon, Ann. der Phys. **65**, 697 (1921);
Suhrmann, Ann. der Phys. **67**, 43 (1922);
Tucker, Phys. Rev. **22**, 574 (1923).
[3] Millikan, Phys. Rev. **18**, 236 (1921)
[4] Hermann, Verh. d. Deutsch. Phys. Ges. **14**, 557, 573, 936 (1912)
[5] Leigh Page, Am. Jour. Sci. **36**, 501 (1913)
[6] Richardson, The Emission of Electricity from Hot Bodies, London 1916, pp. 32, 41.

where ϕ is the increase of energy which accompanies the transference of an electron from the interior of a metal to a point outside, ϕ' and ϕ'' being the values for two different metals. T denotes the absolute temperature, k Boltzmann's constant, e the charge of an electron, σ the coefficient of the Thomson effect, and V the contact difference of potential between the two metals. The term $eT\, \partial V/\partial T$ may also be written eP, P being the Peltier coefficient. The terms $e\sigma$ and $eT\, \partial V/\partial T$ are, in general, small compared with the other terms in the equations. As Bohr[7] has pointed out, P and σ are not identical with the coefficients found by experiment, but this fact is of little importance for the present considerations.

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 ϕ_p is the gain in potential energy and ϕ_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 equal to that of a monatomic gas, we have $\phi_k = (3/2)kT - E_k$.

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

$$(V_s + V_F)e = h\nu - h\nu_o, \tag{3}$$

where V_s denotes the stopping potential, and V_F the contact difference of potential between emitter 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, and if we disregard the fact that the kinetic energy is not the same for all the free electrons, then the largest possible value of the kinetic energy of a photo-electron escaping from the metal must be approximately $E_k + h\nu - \phi_p$. The frequency ν_o for which this is zero is the threshold frequency, and we have

$$h\nu_o = \phi_p - E_k. \tag{4}$$

Instead of using this expression for $h\nu_o$, Millikan[3] placed $h\nu_o$ equal to ϕ' a value which is $(3/2)kT$ larger. This, however, did not influence his result for relative values 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

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

[7] Bohr, Phil. Mag. **23**, 984 (1912)

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

$$- (V_s' - V_s'') + T \, \partial V / \partial T = 0. \tag{5}$$

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 his experimental result that the stopping potential does not depend upon the nature of the emitter. From (5), however, it will be seen that *accurate measurements of stopping potentials should reveal slight differences approximately equal to the Peltier coefficients, expressed in volts.* 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 $h\nu_o$ 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 of 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, but this does not seem to be in accord with observations.

The hypothesis that a quantum of light energy can be transferred entirely to a free electron may seem rather strange. It may, therefore, be worth while to note that it may be reached 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 a 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 free electron.

2. Temperature Variation of the Long Wave-length limit

The influence of a change in temperature upon the threshold fre-
quency ν_o may be found immediately from the theory discussed above,
since $\phi = \phi_p + (3/2)kT - E_k$, Eq. (1) may be written $\partial(\phi_p - E_k)/\partial T = -e\sigma$;
but $\phi_p - E_k = h\nu_o$, hence

$$\partial(h\nu_o)/\partial T = -e\sigma \tag{6}$$

or

$$\partial\lambda_o/\partial T = (\lambda_o^2/hc)\, e\sigma, \tag{6a}$$

$\lambda_o = c/\nu_o$ being the long wave-length limit.

*The temperature variation of the threshold frequency or of the long wave-
length limit is thus proportional to the Thomson coefficient.* Since the Thom-
son effect is always very small, the long wave-length limit should be
practically independent of temperature. For aluminum Borelius and
Gunneson[8] have found $\sigma = -0.56$ microvolts per degree at $400°$K, while
$\lambda_o = 2700$ A. Substituting these values we get $\partial\lambda_o/\partial T = 3.3\times10^{-4}$ 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 σ and λ_o
are measured, (6a) 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
σ is large, as indicated by the values found for the specific heats, and since
λ_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 tempera-
ture upon the photo-electric current.

3. Experimental Method and Apparatus

A variation in 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 measurement of a change would require observations
with different wave-lengths. If photo-currents are found to be constant,
it may be reasonably inferred that the long wave-length limit is indepen-
dent of temperature.

[8] Borelius and Gunneson, Ann. der Phys. 65, 520 (1921)

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°C by water cooling. In tube A, with which most of the experiments with
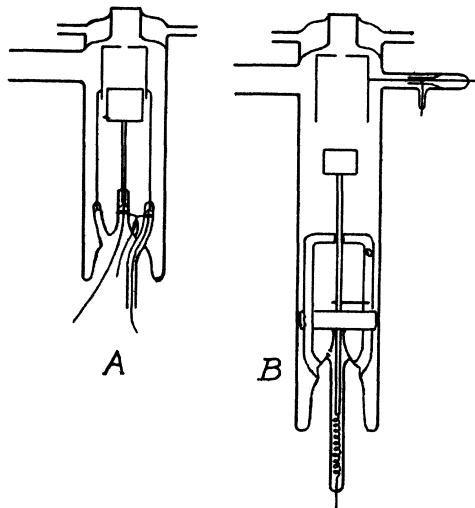

A *B*

Fig. 1. Photo-electric tubes used.

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. To begin with, both tubes had thermo-couples for measuring 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 theimo-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 illumi-
nator 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 covered the slit. The light then just filled
the collimator lens. Under these circumstances the variations in the
intensity of illumination were found to be practically negligible. The
photo-electric tube was set up vertically so that the quartz window was
only a few millimeters from the other slit of the illuminator, the slit in
the receiver being large enough to let the slightly divergent light 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 high 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 1m. 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 the aluminum had been exposed to air, or when it
had been kept for a long time in a vacuum without being heated, the
photo-current was small. A short heating, however, produced a consider-
able increase in the current; and as the heating was continued and the
temperature raised, the photo-current reached a maximum, decreased and
then increased again until a value of 5 or 10 times the original was reached.
Further heating to a temperature close enough to the melting point
produced 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 further change of the photo-current. In one case the follow-
ing values of the current for 2537 A were obtained during the process of
cleaning up, the target being heated several times be+ween 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 remained strong
after prolonged heating at the melting point is an evidence against a
fundamental dependence of the photo-effect upon surface impurities,
although, of course, the heating had not produced a complete clearing-up
of the aluminum surface. Aluminum oxide, for example, cannot be re-
moved by heating. Close to the melting point, 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 connection with the
problem of 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 a charcoal tube between the photo-electric tube and the pumps,
leaving liquid air only on a trap closer to the pumps, a considerable
decrease in the current would immediately set in, amounting to about
30 per cent of the original 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 then generally 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 2 or 3 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 temperature 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 (A and B)
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 temperature 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 1½ hours, 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.
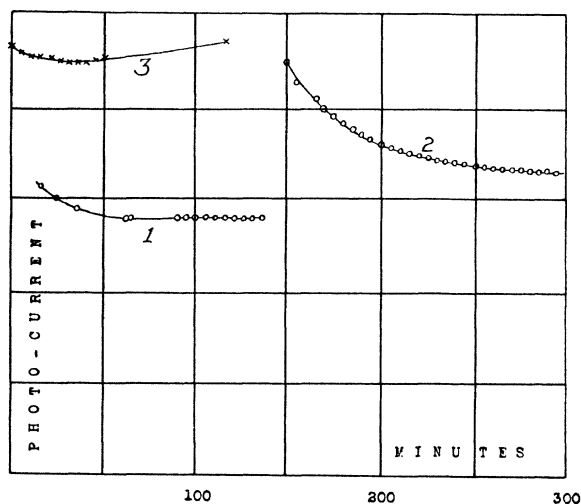

Fig. 2. Photo-currents from aluminum during cooling.

Table I (C) 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 electro-meter zero was determined two minutes before and two minutes after each reading, and corrections were made for a slow motion of the zero amounting to 1.4 cm per hour. Almost no variation 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 ½ per cent.*

TABLE I

Photo-current from aluminum for 2537A

(A)		(B)		(C)	
Time	Photo-current	Time	Photo-current	Time	Photo-current
110 min.	28.20 cm	120 min.	28.13 cm	0 min.	17.2 cm
111	28.18	121	28.12	10	17.3
112	28.15	122	28.15	20	17.35
113	28.14	123	28.10	30	17.29
114	28.11	124	28.13	40	17.30
115	28.13	125	28.15	50	17.33
116	28.12	126	28.10	62	17.6
117	28.15	127	28.20	70	17.8
118	28.15	128	28.12	80	18.0
119	28.14	129	28.14		

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 ½ 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 ½ 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.[9]

5. 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

[9] See Hallwachs' article in Handbuch d. Radiologie, Vol. III.

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 I was taken the target had been heated for 15 minutes at 1300-1400°C.   Curve II was obtained right after Curve I, the target having been heated for 40 minutes between the two sets of readings.   Though the current varies considerably during the
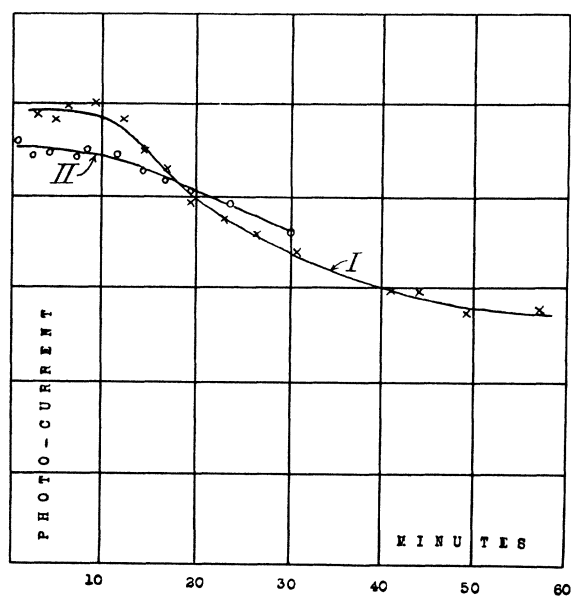

Fig. 3.   Photo-currents from nickel during cooling.

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.

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

NORMAN BRIDGE LABORATORY,
    CALIFORNIA INSTITUTE OF TECHNOLOGY,
       December, 1923.[10]