XLV. The photoelectric effect.—II

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XLV. *The Photoelectric Effect*.—II. By KARL T. COMPTON
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INTRODUCTION.

THERE are two lines of experimental investigation which have been followed in the search for the ultimate explanation of the photoelectric effect from metals. Most of the work in this subject has had to do with the *velocities* of the emitted electrons and the relation of these velocities to the nature of the emitting metal and the frequency and intensity of the incident light. Numerous experimenters have shown that the velocities of the electrons are independent of the intensity of the incident light, and are nearly, if not entirely, independent of the photoelectric fatigue, except in so far as this fatigue alters the intrinsic potential of the metal †, and therefore alters the amount of energy lost by the electrons in escaping. It has therefore been possible to investigate the relation between velocity and frequency without having to take special means of allowing for these two factors. To this extent the investigation of photoelectron velocities is free from complications which are troublesome when the number of emitted electrons instead of their velocities is being studied. This line of investigation has therefore received the most attention.

* Communicated by the Authors.

† K. T. Compton, *Phil. Mag.* vol. xxiii. p. 579 (1912).

Recent work by the writers* and by Hughes† has well established the fact that there is a linear relation between the maximum initial kinetic energy of the emitted electrons and the frequency of the incident light. This relation has been suggested before, but secondary effects due to reflected light and reflected electrons, to impurity of the spectrum, and several other factors have rendered the experimental proofs of this relation uncertain and contradictory. The relation may be expressed by the formula

$$V = k\nu - w_0,$$

where V is the maximum initial kinetic energy of the liberated electrons, expressed in equivalent volts, k and w_0 are constants, and ν is the frequency of the incident light. The average value of k for eight different metals we found to be

$$k = \frac{300}{e} 5.4 \cdot 10^{-27} \text{ erg sec.},$$

while Hughes found

$$k = \frac{300}{e} 5.6 \cdot 10^{-27} \text{ erg sec.}$$

as the average for a number of metals. w_0 is the work, expressed in equivalent volts, done by an electron in escaping from the metal. Our work showed that, within the limits of experimental error, w_0 for any metal has a value which may be calculated independently from a direct knowledge of w_0 for platinum and the contact difference of potential between platinum and the given metal.

These experimental results confirm the theory of photo-electric action which was recently developed by one of the writers‡. By thermodynamic and statistical methods the conclusion was reached that the relation between velocity and frequency should be given by the equation §

$$V = \frac{300}{e} h\nu - w_0, \quad . \quad . \quad . \quad . \quad . \quad (1)$$

where h is Planck's constant, $6.55 \cdot 10^{-27}$ erg sec. The

* Phil. Mag. vol. xxiv. p. 575 (1912).

† Phil. Trans. Roy. Soc. London, A. vol. ccxii. p. 205 (1912).

‡ O. W. Richardson, Phys. Rev. vol. xxxiv. p. 119 (1912); Phil. Mag. vol. xxiii. p. 615 (1912); vol. xxiv. p. 570 (1912); Science, vol. xxxvi. p. 57 (1912).

§ The factor $\frac{300}{e}$ appears throughout this paper because the practical system of electrical units is employed.

theory also led to an expression connecting w_0 for two metals s and p of the form *

$${}_s w_0 - {}_p w_0 = V_p - V_s - \theta \frac{\partial}{\partial \theta} (V_s - V_p), \quad . \quad . \quad . \quad (2)$$

where $V_p - V_s$ is the contact difference of potential between the metals, expressed in volts. The term involving the absolute temperature θ expresses the Peltier effect, and may be neglected in comparison with $V_p - V_s$. The theoretical and experimental values of w_0 agree fairly well. The fact that k is considerably less than the theoretical value h is probably not due to manipulative error, but to experimental error of a more insidious nature. On the whole, however, the support of the theory is consistent and satisfactory.

The second line of attack on the photoelectric problem is the investigation of the effect of the intensity of the light, the frequency of the light, and the nature of the metal on the number of electrons emitted in unit time. Lenard † and others have shown that the number of emitted electrons is simply proportional to the intensity of the incident light. As to the influence of the nature of the metal, it is known in a general way that the more electropositive metals give larger photoelectric currents. It is also known that the slightest oxidation or other chemical action on the illuminated surface of the metal greatly decreases the size of the photoelectric currents. This "fatigue" is prevented in proportion as a perfect vacuum is approached. Except for the work of Pohl and Pringsheim, which will be discussed later, little is known concerning the relation between the frequency and the rate of emission of electrons except the fact that photoelectric currents apparently increase as shorter wave-lengths of light are employed ‡.

The theory of photoelectric action developed by one of the writers § yields an expression connecting the frequency, nature of the metal, and number of electrons emitted in unit time, as well as the expression for the initial kinetic energy already referred to. The complete theory leads to the following equations:

$$N=0 \text{ when } 0 < \frac{300}{e} h\nu < w_0, \quad . \quad . \quad . \quad (3)$$

* O. W. Richardson, *Phil. Mag.* vol. xxiii, p. 264 (1912); vol. xxiii, p. 615 (1912).

† *Ann. d. Phys.* vol. viii, p. 149 (1902).

‡ Hallwachs, *Ann. d. Phys.* vol. xxx, p. 593 (1909).

§ *Op. cit.*

$$N = \frac{Ah}{R^2\nu^2} \left(1 - \frac{ew_0}{300h\nu}\right) \text{ and } V = \frac{300}{e} h\nu - w_0$$

$$\text{when } w_0 < \frac{300}{e} h\nu < 0. \quad . \quad . \quad (4)$$

In these equations N is the number of electrons emitted per unit area per unit time by light of unit intensity, A is a constant characteristic of the metal, and R is the absolute gas constant reckoned for one molecule. The other symbols have the meanings assigned to them previously.

An examination of the expressions for N shows several facts in support of the theory. There is apparently a critical frequency, given by

$$\nu_0 = \frac{w_0}{h} \frac{e}{300}, \text{ or } \lambda_0 = \frac{300}{e} \frac{h}{w_0} c, \quad . \quad . \quad (5)$$

below which there is no photoelectric emission.

This we found to be true. The agreement on this point between theory and experiment is illustrated by Table I.,

TABLE I.

Metal.	λ_0 observed.	λ_0 calculated.
Na	577 $\mu\mu$	550 $\mu\mu$
Al	360	360
Mg	375	390
Zn	357	340
Sn	337	305
Bi	337	290
Cu	309	275
Pt	280	270

which shows the values of the critical wave-lengths for eight metals. The calculated values of λ_0 are obtained from equations (5) and (2), taking w_0 for platinum to be 4.7 volts*, and using values of the contact difference of potential of each metal with respect to platinum as taken from standard tables. The observed values are a little uncertain, since the photoelectric currents are small in this region, and since we used a quartz-mercury arc, which gives a discontinuous spectrum. However, we determined λ_0 as best we could under the circumstances. Some of these values were determined during the course of this investigation. The rest are

* H. L. Cooke and O. W. Richardson, Phys. Review [2] vol. i. p. 71 (1913); Phil. Mag. vol. xxv. p. 624 (1913).

taken from our last paper. Considering the fact that the intrinsic potentials of the investigated surfaces may have been somewhat different from the values given in the tables, and since the finite size of the spectrometer-slits caused a slight overlapping in the spectrum, these results are in very fair support of the theory.

We have, therefore, good experimental support of those results of the theory expressed by

$$N=0, \text{ when } 0 < \frac{300}{e} h\nu < w_0$$

$$\text{and } V = \frac{300}{e} h\nu - w_0, \text{ when } w_0 < \frac{300}{e} h\nu < 0.$$

There still remains to be tested the equation

$$N = \frac{Ah}{R^2\nu^2} \left(1 - \frac{e}{300} \frac{w_0}{h\nu} \right), \text{ when } w_0 < \frac{300}{e} h\nu < 0. \quad (6)$$

The purpose of this paper is the experimental investigation of the relations involved in this equation.

Preliminary Considerations.

At the outset it should be remarked that equation (6) is not necessarily the only or the complete expression of the theory. The thermodynamic and statistical treatment yielded two integral equations which were not satisfied by any analytic function continuous throughout the entire range of variation. It was found, however, that equations (3) and (4) are a solution of these integral equations. The complete solution may therefore consist of the sum of several terms, of which equation (6) is only one part. This suggestion will be considered again later in the paper. It is also possible that the approximations used lead to an error in this part of the solution.

One evident requirement of the theory is that the rate of photoelectric emission must reach a maximum at some particular frequency, instead of increasing indefinitely with the frequency as was at first supposed. For from equation (6)

$$\frac{dN}{d\nu} = \frac{Ah}{R^2\nu^3} \left(\frac{e}{300} \frac{3w_0}{h\nu} - 2 \right) = 0,$$

$$\text{whence } \nu_{\max.} = \frac{3}{2} \frac{e}{300} \frac{w_0}{h} = \frac{3}{2} \nu_0, \quad (7)$$

$$\text{and } \nu_{\min.} = \infty \quad (8)$$

$$\frac{d^2N}{d\nu^2} \text{ is } \begin{cases} \text{negative when } \nu = \frac{3}{2} \nu_0 \\ \text{positive when } \nu = \infty \end{cases}$$

Therefore equation (6) requires the photoelectric sensitiveness of any metal to be a maximum at a wave-length equal to $\frac{2}{3}\lambda_0$, where λ_0 is the longest wave-length at which electrons are emitted, and it requires that the sensitiveness approach zero when the wave-length is exceedingly small.

The existence of a maximum in the curve representing the relation between frequency and rate of emission is proved by the work done on a large number of metals by Pohl and Pringsheim*. The results of their experiments may be generalized in the statement that the wave-length-rate of emission curve for every metal is of the type shown in fig. 1, *abcde*, and that for each metal the starting-point and the position of the maximum are at wave-lengths peculiar to the given metal. *N* is the number of electrons emitted

Fig. 1.

per second by a unit amount of light-energy. They find that the part *bcd* of the curve is present only when there is a component of the electric intensity in the light-wave which is perpendicular to the mirror surface of the metal. When the light is incident perpendicularly the part *bcd* degenerates into the dotted line *bd*, which forms part of a continuous curve *abd*. This curve is not in good agreement with equation (6), which is represented by the curve *afcg*. However, the theoretical curve *afcg* was obtained on the supposition that the radiation incident on the metal is isotropic, while the experimental curve of Pohl and Pringsheim was obtained with the light incident at a certain definite angle. They found that the relative importance of the "hump" *bcd* depends greatly on the angle of incidence. Therefore these curves are not strictly comparable.

However, Pohl and Pringsheim found that the position of the maximum is nearly or entirely independent of the angle

* *Verh. d. D. Phys. Ges.* vol. xiii. p. 474 (1911); vol. xii. p. 349 (1910); vol. xii. p. 682 (1910); vol. xiv. p. 46 (1912), &c.

of incidence. Therefore we may use their data on the wavelength at which the photoelectric emission is a maximum for various metals, and compare these results with the requirements of the theory expressed by equation (6), or rather, by equation (7). This comparison is shown in Table II. The calculated values of $\lambda_{\max}$ are obtained from equation (7), taking w_0 for each metal as given by equation (2), taking values of the contact difference of potential with respect to platinum from standard tables, and taking for platinum $w_0=4.7$ volts. The observed values of $\lambda_{\max}$ are taken directly from Pohl and Pringsheim's papers. The blank spaces represent cases in which the data are not available and are put in because they may be of interest later.

TABLE II.

Metal.	$\lambda_{\max}$. calculated.	$\lambda_{\max}$. observed.
Rb	...	475 $\mu\mu$
K	404 $\mu\mu$	440
Na	367	335
Ca	...	360
Ba	...	280
Li	...	280
Mg	260	250
Al	240	247.5
Zn	223	...
Sn	200	...
Cu	184	...
Pt	180	...

Wherever comparison is possible the agreement with the theory is quite good. Pohl and Pringsheim did not determine points close together on their curves, and the exact positions of the maxima are doubtful within limits large enough to account for most of the discrepancies in the table.

The most obvious discrepancy between the theoretical equation and the curves of Pohl and Pringsheim is that the sensitiveness in the region of very short wave-lengths is increasing as the wave-length decreases, while the theory requires that it should finally fall to zero. The further experimental test of the theory, as expressed by equation (6), which we shall now proceed to describe, differs from the work of Pohl and Pringsheim principally in the fact that we secure approximate isotropic monochromatic radiation falling on the strip, and that we extend the measurements farther out into the ultra-violet than has hitherto been done.

The apparatus which we found most satisfactory for making the photoelectric measurements is illustrated in fig. 2. It is similar to that used in our previous experiments

on electron velocities, with the addition of arrangements designed to make possible a more perfect vacuum and to give an absolutely clean, untarnished metal strip upon which to focus the light from the spectrometer-slit. Light from the

Heraeus quartz mercury arc-lamp Q entered the collimator-slit of a Hilger monochromatic ultra-violet illuminator and entered the photoelectric cell through a quartz window P. The apparatus was adjusted so that the light from the slit was exactly focussed on the strip S of metal to be tested, so that the strip and the image of the slit exactly coincided for each wave-length of light. The wave-length of light falling on the strip was shown directly by the graduated drum W. The degree of adjustment could be examined by looking into the bulb at G. The requisite vacuum was obtained by first using a Gaede pump, then sealing off the pump connexion at F and immersing the tube of coconut charcoal R₁ in liquid air. Under the influence of the light, electrons escaped from the strip S to the inside silvered surface of the bulb B. The rate of emission of electrons was measured by observing the rate of deflexion of the electrometer E, which was connected with the strip S. The bulb B was maintained at a positive potential of 5 volts (contact difference of potential being allowed for). This gave complete saturation and prevented any reverse current from B to S due to light reflected from the strip S to the walls of the bulb B.

It has been mentioned that the theory is based on the assumption that isotropic radiation falls upon the metal strip. Since the light falling upon the strip in our apparatus was practically a parallel beam, we secured the equivalent of the incidence of isotropic light by bending the strip around a lengthwise axis into such a shape that, with a parallel beam of light striking it, there would be the same proportion of light incident at each angle as if isotropic radiation were incident on a plane surface. We determined graphically the shape of cross-section of the strip necessary to fulfil these conditions, and found that it is approximately elliptical, with the major axis twice the minor axis, and pointing in the direction of the light.

In order to obtain absolutely fresh metal surface for the photoelectric tests we adopted the following device. The metal strip S, of elliptical cross-section and just the size of the image of the slit, was fixed to the end of a light aluminium rod R which was capable of a motion up and down in a closely fitting brass tube. Stops D were arranged so that the upper limit of motion brought the strip exactly in the path of the light, while the lower limit left the strip inside of a small bulb T directly below the main bulb B. The brass tube was firmly waxed into the outer glass tube at A. A soft iron block I was attached to the upper end of the aluminium rod, so that the strip could be moved up or down

at will by sliding an electromagnet up or down outside of the apparatus. A suspending spring C was just strong enough to keep the strip in its regular position when the electromagnet was removed. A bit of the metal to be investigated was placed in the quartz furnace H, which was wound with a platinum heating-coil. After the requisite vacuum had been obtained, the strip S was drawn into the bulb T and the metal distilled from the furnace over on to the strip, where a thin film of the metal to be investigated was deposited. Then the strip was returned to its position in the bulb B, and photoelectric measurements were made as soon as possible. This method worked very satisfactorily, and can be used for most metals which melt below about 1000° C.

This was the apparatus used in testing sodium. The low melting-point of caesium made a variation of this process more convenient. The caesium, after being washed in anhydrous ether, was placed in the small bulb K, which was at once sealed on to the tube ML. After a liquid-air vacuum had been maintained for several hours the caesium was melted so that it flowed successively through the constrictions at M and L. The caesium oxide and other impurities were left behind at L, and the tube was sealed off at M with a blowpipe. Then the caesium was distilled on to the strip by gently heating the bulb T. This method proved very satisfactory, for the caesium gave practically constant photoelectric currents during the time necessary to complete a test.

These precautions were not taken when aluminium and platinum were tested, although in the case of aluminium we should probably have obtained better results had we taken them. In these cases the metal strip was scraped with a clean knife-blade in air, quickly placed in position, and the vacuum pump started. Certainly some oxidation of the aluminium surface occurred before the vacuum was obtained.

As soon as the strip S was ready for the test the drum W was turned so as to cause light of different wave-lengths to fall successively on the strip. For each wave-length we measured the deflexion of the electrometer in some definite interval of time, say ten seconds. Thus data were obtained giving, in arbitrary units, the number of electrons liberated in unit time from the metal by the light of each wave-length represented in the spectrum of the mercury arc. But in order to apply these results to test equation (6) it was necessary first to make a correction for the fact that the various lines in the arc spectrum were not all of equal intensity. This necessitated a calibration in order to find the relative energies in different parts of the spectrum. Then, when the

number of electrons liberated per unit time by light of each wave-length was divided by the energy of the light of the corresponding wave-length, the quotient represented the relative number of electrons liberated in unit time by a unit amount of light-energy for each wave-length. These values may be used directly to test equation (6). They are called N in the curves and are plotted as ordinates.

The Energy Calibration.

The relative energies in different parts of the spectrum were measured by means of a bismuth-silver linear thermopile made by W. W. Coblentz*. This thermopile was adapted to the monochromatic illuminator and was placed directly back of the slit in the telescope arm. This slit was adjusted to the exact width and position of the strip which had been tested photoelectrically. The energy was determined by a compensation method illustrated in fig. 3. The thermopile

T was connected in series with a shunt S and a Thomson astatic galvanometer G . A second circuit contained, in series, the shunt S , a battery B , and a variable resistance R . The battery was connected so that its electromotive force opposed that generated by the thermopile. The resistance R was adjusted so that no current flowed through the galvanometer. Under these conditions the radiation energy falling on the thermopile was inversely proportional to the resistance R . For the current through the battery is

$$I = \frac{E}{R + b + \left(\frac{1}{\frac{1}{s} + \frac{1}{t + g}} \right)},$$

where E is the electromotive force of the battery, and b , s , t , and g are the resistances of the battery, shunt, thermopile, and galvanometer respectively. R varied from 20,000 to 1,200,000 ohms in different parts of the spectrum, b and s were each 0.01 ohm, t was 8 ohms and g was 10.5 ohms.

* Franklin Inst. Journ. clxxv. p. 151 (1913).

Therefore we may neglect all of the resistance except R , and write

$$I = \frac{E}{R}.$$

The drop across S was

$$d = I_s = \frac{E_s}{R} = \frac{K}{R},$$

where K is a constant. When the resistance R was adjusted so that no current passed through the galvanometer, obviously

$$\frac{K}{R} = e,$$

where e is the electromotive force generated by the thermopile. Thus the electromotive force was inversely proportional to the resistance R . But the electromotive force is proportional to the rise in temperature, which in turn is proportional to the energy of the incident light. Therefore the reciprocal of the resistance required for compensation was a measure of the energy of the light incident on the strip.

By this method the galvanometer was a detector only, and the measurements were independent of any changes in its sensitiveness. For measurements in the extreme ultra-violet between wave-lengths $200\ \mu\mu$ and $250\ \mu\mu$ the sensitiveness of the galvanometer was about 5×10^{-11} ampere per division. In the rest of the spectrum it was unnecessary to maintain such high sensitiveness.

The calibration of the spectrum was repeated at intervals during the course of the investigation. It was found that, for a given number of amperes running through the arc-lamp, the energy distribution in the spectrum remained practically constant during the period of the three months' investigation. The slight variations that occurred were allowed for.

There is one peculiarity of the apparatus which should be mentioned before taking up the experimental results. The collimator slit, the metal strip, and the slit in front of the thermopile were each $\frac{1}{16}$ inch wide. This large width resulted in considerable overlapping and impurity in the visible part of the spectrum from wave-lengths $400\ \mu\mu$ to $700\ \mu\mu$. But out in the ultra-violet the dispersive power of the instrument was about twenty times as great as in the visible spectrum, so that in this region, which was the most important, the error due to the finite sizes of the slits was negligible. The reason for making the slits so wide was that in the visible spectrum the photoelectric currents were

small and in the ultra-violet the energy was small, so that in both parts of the spectrum it was found best to use fairly wide slits and strips. The effect of this width of slits will be considered when the experimental results are discussed.

Experimental Results.

Platinum.—The experimental results in the case of platinum are given in Table III. λ and ν are the wave-length and frequency of the incident light, d_1 and d_2 are deflexions of the electrometer per half minute, d is the average of d_1 and d_2 , E is the energy of the incident light in arbitrary units, and N is proportional to the number of electrons emitted per unit time by light of unit intensity. The readings were taken in order down the column d_1 and then up the column d_2 . The averages should be relatively independent of any fatigue

TABLE III. *Platinum.*

λ .	ν .	d_1 .	d_2 .	d .	E .	$N = \frac{d}{E}$.
200 $\mu\mu$	150(10) ¹³	34	32	33	1.00	33
202	148.5	31	29	30	1.00	30
204	147	23	24	23.5	0.83	27
214	140	44	40	42	1.7	25
220	136	58	51	54.5	2.0	27
230	130	71	62	66.5	4.1	16
240	125	55	50	52.5	6.3	8.3
254	118	34	31	32.5	24.3	1.5
260	115.5	16	14	15	22.7	0.7
270	111	5	5	5	16.6	0.3
280	107	1	4	2.5	14.5	0.2
290	103.5	0	1	0.5	21.2	0.02
300	100	0	0	0	43.5	0

Fig. 4.

effect. The relation between λ , ν , and N is shown graphically in fig. 4, curve 1. Curve 2 is the graph of equation (6), the ordinates being in arbitrary units.

Aluminium.—Table IV. contains the results of the first set of measurements with aluminium. The absolute values

TABLE IV. *Aluminium.*

λ .	ν .	d_1 .	d_2 .	d .	E.	$N = \frac{d}{E}$.
200 $\mu\mu$	150 (10) ¹³	103	87	95	1.11	85
202	148.5	90	76	82	0.91	90
204	147	85	70	78	0.83	94
208	144	99	92	96	0.91	105
212	141.5	149	130	140	1.25	112
214	140	172	150	161	1.43	113
220	136	249	223	236	2.00	118
224	133.7	319	294	306	2.80	113
226	132.5	343	322	333	2.95	113
228	131.5	363	343	353	3.45	102
230	130	401	385	393	4.20	93
232	129.2	423	406	415	4.75	87
234	128.2	439	430	435	5.30	82
236	127.1	500	481	490	5.90	83
240	125	500	493	497	7.1	70
242	124	531	518	525	7.7	68
254	118	1300	1200	1250	28.5	44
265	113.2	518	512	515	18.5	28
275	109	294	287	290	14.5	20
290	103.5	141	140	140	21.2	6.5
313	95.5	82	78	80	55.5	1.5
339	88.5	17	17	17	29.5	0.6
366	82	7	7	7	77.5	0.09

Fig. 5.

of N for the different metals cannot be compared with each other, since the experimental conditions were usually altered between each test. The curve is shown in fig. 5

(curve 1). Curve 2 is the graph of equation (6), reckoned for aluminium, N being expressed in arbitrary units. The readings for curve 3 were taken 72 hours after those for curve 1. The shrinkage represents the photoelectric fatigue during this interval. Curves 4 and 5 were taken under the same conditions as curve 1, except that the strip S was bent so as to receive the light at perpendicular and acute incidence in the two cases. Apparently the angle of incidence was of little or no influence. It must be remembered, however, that the aluminium strip was scraped with a knife-blade and was far from having a polished plane surface. Therefore this test may indicate little except that there can be no error in curve 1 due to any slight departure of the shape of the strip from its supposed elliptical cross-section.

Sodium.—The results in the case of sodium are shown in fig. 6, curves 1, 2, 3. Experimental difficulties prevented

Fig. 6.

the photoelectric measurements being taken within less than one hour after the sodium had been distilled on to the strip S . Curves 1, 2, and 3 represent the variation of N with ν , 1, $2\frac{1}{2}$, and 18 hours respectively after distillation. Curve 4 represents (6) plotted for sodium, the ordinates being in arbitrary units. The photoelectric currents were about fifty times as large as in the case of aluminium. The experimental results were of exactly the same type as those shown in Tables III. and IV.

Cæsium.—The results in the case of cæsium are illustrated by fig. 7, curve 1. The energy calibration in this case was less satisfactory than in the preceding cases, since the galvanometer was rather unsteady. On the other hand, the photoelectric measurements were exceedingly satisfactory.

Fig. 7.

Evidently the method employed in purifying and distilling the cæsium made possible a better vacuum, and consequently there was less fatigue than in the preceding cases.

Discussion of Results.

The most striking conclusion to be drawn from these results is that there are *two* maxima in the sensitiveness-frequency curve, instead of but one maximum, as indicated by the theory and by the experiments of Pohl and Pringsheim. In the Pohl and Pringsheim curve in fig. 1 we see that the "normal" photoelectric effect, represented by *abcd*, reaches a maximum similar to that reached by the "selective" effect *bcd*, but farther out in the ultra-violet. Experiments with Röntgen rays indicate that the "normal" effect does not increase indefinitely with the frequency. The fact that we were able to discover this second maximum was due to the use of very electropositive metals and to the sensitiveness of our energy calibration system, which enabled the investigation to be carried further into the ultra-violet than ever before.

An examination of the curves for sodium shows that the first maximum (*a*) decreases more rapidly as "fatigue" proceeds than does the second maximum (*b*). This is what we should expect, since the electrons liberated by light in the region of the second maximum possess much greater initial velocities, and are therefore better able to penetrate the surface layer of oxide. Evidently, if measurements could have been made immediately after the sodium had been distilled, the sensitiveness at (*a*) would have been considerably greater than at (*b*).

In the case of platinum, fig. 4, both maxima lie beyond the region in which measurements are possible. The value of λ_0 , about $280\ \mu\mu$, agrees well with the value $270\ \mu\mu$ calculated theoretically.

In fig. 5 for aluminium the first maximum only appears. It is at a wave-length $\lambda_{\max.} = 220\ \mu\mu$, whereas the theory would put it at $240\ \mu\mu$. A possible explanation of this discrepancy is suggested by the fact that the maximum shifts to the right as photoelectric fatigue proceeds, as is seen by comparing curves 1 and 3. This is consistent with the fact, mentioned previously, that metal surfaces become more electronegative and assume properties of more electronegative metals as fatigue takes place. Since the aluminium was in contact with the air for a short while before making the test, it is certain that the true maximum for aluminium is at a wave-length longer than $220\ \mu\mu$. Whether the entire discrepancy may be explained in this way is not known. The value of λ_0 , $360\ \mu\mu$, agrees exactly with that calculated from the theory.

The fatigue in the case of sodium, fig. 5, was less than in the case of aluminium, because much greater pains were taken to secure a good vacuum. There is no certain evidence of any shift of the maxima with time. The first maximum (*a*) is at wave-length $360\ \mu\mu$, which agrees almost exactly with the theory. The second maximum (*b*) is at wave-length $227\ \mu\mu$. Because of the wide slit and strip, and consequent overlapping in the visible spectrum, λ_0 cannot be accurately determined from these curves, and it appears larger than it really is. It is probably not far from the calculated value $\lambda_0 = 550\ \mu\mu$. The large overlapping in this spectral region is shown in fig. 8 (p. 566), which represents the dispersive power of the instrument at different wave-lengths. There is very little overlapping of spectral lines for wave-lengths less than $300\ \mu\mu$. But the overlapping is very considerable in the visible spectrum.

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The most serious effect of this overlapping appears in the case of caesium, fig. 7. Here there is little or no evidence of the first maximum, which theory and analogy would place in the red or infra-red part of the spectrum. It is possible

Fig. 8.

that the maximum lies beyond the range of the illuminator and the mercury arc. If it should lie at a wave-length longer than about 550 $\mu\mu$ it is also possible that it would be masked by the low dispersive power of the instrument in this region. Thus the left end of the curve is unsatisfactory. The second maximum (*b*), however, is shown very distinctly and is at a wave-length of about 250 $\mu\mu$.

Conclusion.

The experimental results indicate that the photoelectric sensitiveness is the same function of the frequency for all metals, the difference being that the curve is shifted bodily out to the region of short wave-lengths for the electronegative metals. This function is evidently not that expressed by equation (6). Equation (6), however, accurately predicts the values of λ_0 and $\lambda_{\max}$, and seems to be at least a part of the truth.

It will be remembered that earlier in the paper reference was made to the fact that equation (6) is only one solution of the theoretical equations, and that it is probably not the only or the complete solution. The results of this investigation point

to the existence of another term in the solution. If this is true, the real expression of the theory should not be equation (6), but an equation in which N equals the sum of two terms. The first term would be the right member of equation (6), or something very similar to it, and would provide the first maximum and account for the "selective" effect. The second term would provide the second maximum and account for the "normal" effect. The discovery of the equation of the relation between frequency and sensitiveness would be of practical as well as theoretical importance, since it would render possible the use of photoelectric cells as the most sensitive of spectrophotometers. We have not succeeded as yet in discovering such a solution of the theoretical equations.

We are glad to take this opportunity to express our thanks to Professor Augustus Trowbridge for many valuable suggestions with regard to the adjustment and use of the galvanometer.

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XLVI. *The Effect of Ionization of Air on Electrical Oscillations and its bearing on Long-Distance Wireless Telegraphy.* By EDWIN H. BARTON, D.Sc., F.R.S.E., Professor of Experimental Physics, and WALTER B. KILBY, B.Sc., "1851 Exhibition" Research Bursar, University College, Nottingham*.

[Plate XI.]

IN his stimulating address before the physical and engineering sections of the British Association at Dundee on Sept. 6, 1912, Dr. Fleming dealt with the various unsolved problems of long-distance wireless telegraphy.

One of the points of outstanding difficulty then commented upon was the mechanism of the propagation of the æther radiation round the curvature of the earth in those cases where about a quarter of its circumference is passed over.

In the subsequent discussion Dr. Eccles brought forward his theory †, which attributes the bending of the waves round the earth to a higher velocity of propagation in the upper regions of the atmosphere, owing to the ionization there present. This increased speed of propagation was

* Communicated by the Authors.

† Proc. Roy. Soc. A. vol. lxxxvii. pp. 79-99 (1912).