

LIII. *The Photoelectric Effect.* By O. W. RICHARDSON
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[Plate XIII.]

PROBABLY there is no line of investigation more likely to lead to a correct understanding of the phenomena of photoelectric action than a careful determination of the relations between the nature of the metal, the frequency of the light, and the kinetic energy of the liberated electrons. A large amount of work has been done in the attempt to determine these relations, but the results have been very contradictory. For instance, von Baeyer and Gehrts †, and Klages ‡ found, in the case of several metals, that the maximum initial velocity of the electrons was independent of the metal used. Ladenburg § and other physicists have decided that the electronegative metals give off electrons with the greatest velocities; whilst Millikan and Winchester || concluded that the initial velocity bears no relation to the Volta series. Most physicists who have investigated the subject believe that the maximum initial kinetic energy is a linear function of the frequency of the light; but some ¶ have obtained results supporting the view that the maximum velocity varies as the first power of the frequency.

The results of the present investigation show that there is a much greater unity in the relations between different metals and wave-lengths than has hitherto been supposed. In fact, it will be shown that the important features of the photoelectric behaviour of any metal are determined by a single parameter characteristic of the metal. The parameter has the dimensions of a frequency, and its significance will be explained later.

The first part of the paper is a discussion of the experimental data. These data may be of value in testing any theory of photoelectric action. In the latter part of the paper the results are applied to test the theories of these effects which have been developed by Einstein ** and by one of the authors ††.

* Communicated by the Authors.

† *Ber. der Deutsch Physik. Ges.* xxi. p. 870 (1910).

‡ *Ann. der Physik*, vol. xxxi. p. 343 (1909).

§ *Verh. der Deutsch Physik. Ges.* ix. p. 504, *ibid.* p. 165 (1907); *Phys. Zeits.* vol. viii. p. 592 (1907).

|| *Phil. Mag.* vol. xiv. p. 185 (1907).

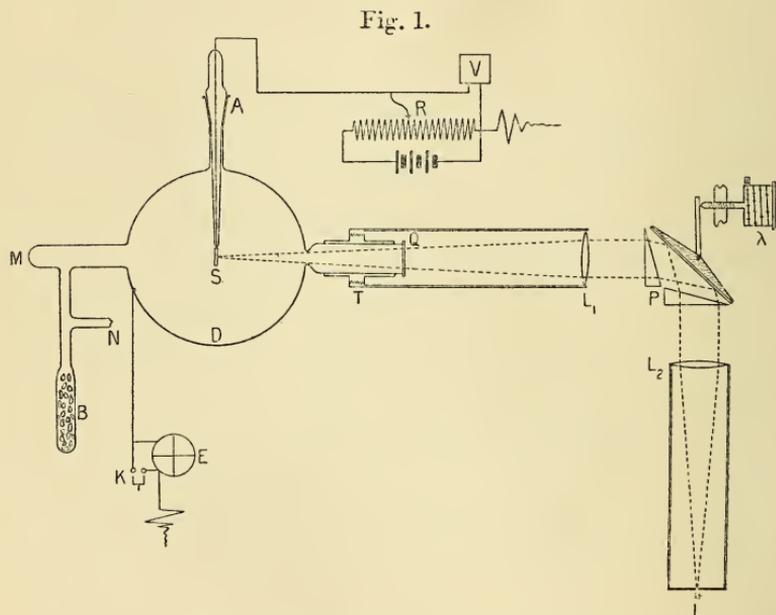
¶ Kunz, *Phys. Rev.* vol. xxxi. p. 536 (1910), vol. xxxiii. p. 208 (1911).

** *Ann. der Physik*, vol. xvii. p. 146 (1905).

†† *Phys. Rev.* vol. xxxiv. p. 146 (1912); *Phil. Mag.* vol. xxiii. p. 615 (1912); *Science*, vol. xxxvi. p. 57 (1912).

The main points wherein the present investigation differs from the earlier work on this subject are as follows:— (1) The contact difference of potential between the emitting and receiving electrodes is allowed for*. (2) The photoelectric cell is placed in position in an arm of a new type of monochromatic ultra-violet illuminator, made by Adam Hilger Ltd., of London, which is a distinct advance as a method of producing accurate and powerful illumination by monochromatic ultra-violet light. (3) The peculiar form of the photoelectric cell practically eliminates electron reflexion without the use of a screen and an auxiliary field, and at the same time it enables the distribution of total kinetic energy to be measured instead of simply the distribution of the velocity component normal to the emitting electrode.

The apparatus used is shown in fig. 1. The emitting electrode consists of a strip *S* of metal foil about 1 mm. wide and 5 mm. long placed at the centre of a glass bulb *D* of



7.5 cm. diameter. This bulb is silvered on its inner surface. It is connected with an electrometer having a sensibility of 936 divisions per volt, and acts as the receiving electrode. The strip *S* is held in position by a thin platinum wire sealed in a small glass tube, and is introduced through the ground-

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

glass joint A. The neck of this bulb is closed by a quartz window Q. It is waxed firmly in a brass collar which screws into the telescope tube of the monochromatic illuminator at T, in such a position that the slit L is just focussed on the strip S so that the image of the slit for any particular wave-length of light may be made to coincide with the position of the strip. The final adjustment is made by using visible light as the source and looking through M. The strip S is shifted a little until it just shuts out the image. By turning the screw-head λ any desired wave-length may be thrown on S and its magnitude read off on the graduated scale. In the figure the illuminator is shown rotated through a right angle from its true position, about the axis of the telescope. The collimator should project out perpendicular to the plane of the paper. A quartz mercury lamp at L was used as the source of light. The apparatus was evacuated by a Gaede pump connected at N, and usually the tube B of coconut charcoal was used to obtain a still better vacuum.

The velocities of the liberated electrons were determined by varying the field between S and D by adjusting the sliding contact R, and the applied field was read directly from the voltmeter V. The distribution of velocity curves were obtained in the ordinary way.

The peculiarities of this apparatus are that the field between S and D is approximately radial, and that the area of the emitting electrode is very small compared with the area of the receiving electrode. In the first place, this arrangement makes it possible to measure the distributions of velocity of all the electrons irrespective of their angles of emission from S, and thus it gives the distribution of total energy of the electrons. In the second place, it makes the effect of electron reflexion practically negligible. A certain percentage of the electrons reaching D are reflected, this reflexion being diffuse. But none of these reflected electrons will return to S, except a very small proportion which start almost straight towards S. All the others will traverse comet-like paths past S and again strike D.

The metal strip to be tested was carefully scraped with a clean knife-blade. It was then placed quickly in position and the vacuum-pump started. The readings were taken as soon as the requisite vacuum was obtained.

The Distribution of Velocities.

The general character of the distribution of velocity curves is the same for all the metals, so that it will be sufficient to consider in detail the case of platinum only. With this

metal readings were taken for wave-lengths 25, 23, and 21. The unit of wave-length is 10^{-6} cm. The readings are shown in Table I. V is the externally applied potential difference, R is the deflexion in scale-divisions per minute, and C is this deflexion reduced to a scale of 100 for the maximum deflexion. These readings may be taken as typical of all the distribution of velocity curves that we have obtained.

It is necessary to correct these readings for contact difference of potential. The method of determining this correction will be described later. After being thus corrected the numbers in Table I. are plotted thus:— \circ in fig. 2 (Pl. XIII.). The significance of these curves may be explained as follows:—Take, for instance, the curve for 23 λ . The ordinate at -0.5 volt is 44. This means that 44 per cent. of the electrons are liberated with velocities equal to or greater than that velocity which gives them sufficient energy to overcome an opposing difference of potential of 0.5 volt.

TABLE I.

V.	$\lambda = 25.$		$\lambda = 23.$		$\lambda = 21.$	
	R.	C.	R.	C.	R.	C.
+ 2	41	98	78	100	31	100
1	42	100	78	100	31	100
0.5	41	98	78	100	31	100
0.2	42	100	78	100	31	100
0.1	42	100	78	100	31	100
0.05	42	100				
0.0	40	95	76	97	30.5	98.5
- 0.1	27	64	68	87	29	93
0.2	9	22	54	69	26	84
0.3	3	7	44	56.5		
0.4	0	0	30.5	39	21	68
0.5	19	24		
0.6	8	10	15	48
0.7	1.5	2		
0.8	0	0	8.5	27
0.9	6.5	19
1.0	3	10

To obtain the relative number which are emitted with any given energy, we must differentiate these curves with respect to V . The result of this differentiation is shown in fig. 3. For wave-length 25 the number emitted with an energy corresponding to 0.2 volt is to the number corresponding to 0.1 volt as the ordinate in fig. 3 at 0.2 volt is to the ordinate at 0.1 volt, or as 90 is to 65, and so on.

An examination of these curves leads to a number of interesting conclusions.

(1) The maximum energy, expressed in volts, is a linear function of the frequency of the exciting light, within the limits within which the results of the experiments are consistent.

(2) The curves appear to be almost symmetrical with respect to their maximum ordinates. This shows that if the maximum energy is a linear function of the frequency, the average energy, which is equal within the limits of experimental error to the most probable energy, also bears a linear relation to the frequency.

(3) The curves intersect the voltage axis at finite angles, both at the end which corresponds to zero energy and at the end which corresponds to the maximum energy.

(4) If the wave-length is increased to a certain value, which is in the neighbourhood of $\lambda = 27$ in the case of platinum, the distribution of velocity curve will degenerate into a straight line coincident with the current axis. The photoelectric currents in this region were too small to permit of such a curve being obtained, but the experiments show that this limiting wave-length, which we may call λ_0 , has a particular meaning. It is the longest wave-length that will produce any photoelectric effect from the metal under investigation, and the electrons emitted by this light are emitted with zero velocity. This wave-length λ_0 , or the equivalent frequency ν_0 , is that constant which has already been alluded to which determines the photoelectric properties of the metal.

Analysis of the Distribution of Velocity Curves.

Since the curves in fig. 3 show that the mean velocity of the emitted electrons is very close to the most probable velocity, it might be thought that the mean velocity should be the characteristic velocity received by the electrons under the primary influence of the light. The deviations from the mean would then be due to collisions with other electrons in the matter traversed, some of the emitted electrons losing and others gaining energy in this way. The results can, however, be equally well interpreted on the view that all the collisions in the interior of the matter result in a diminution of the energy of the emitted electrons. We shall limit the discussion to the case of a beam of light incident normally to the emitting surface.

Let each electron which is set free from its parent atom or equivalent system in the interior under the influence of

the monochromatic radiation have a constant amount of kinetic energy T_0 . We shall assume that this energy diminishes to $T_0 F_2(r)$ when the electron has traversed a distance r inside the matter from its point of origin, and in addition that it has to do a definite amount of work P in order to escape from the surface. The energy T of the electrons which originate at a distance r from the point where they escape from the surface is then a function of r only. It is given by

$$T = T_0 F_2(r) - P. \quad (1)$$

Consider all the electrons which emerge from an element dS of the surface, and which originate at a distance between r and $r + dr$ from the point of emergence. Let θ be the angle between the radius r and the internal normal to dS . Let λ_1 be the coefficient of extinction of the light with distance. Then the number of electrons which originate in an element of volume $d\tau$ at a depth defined by r and θ will be $e^{-\lambda_1 r \cos \theta} A d\tau$, where A is a constant. In addition to losing energy the electrons will diminish in number with the distance traversed in the matter. Let the proportion which disappears in this way in a distance r be $1 - F_1(r)$. Then the total number which reach dS and which come from a distance between r and $r + dr$ is

$$\begin{aligned} dN &= \int_{-\pi/2}^{\pi/2} e^{-\lambda_1 r \cos \theta} A \cdot 2\pi r^2 \sin \theta dr F_1(r) \frac{dS \cos \theta}{r^2} d\theta, \quad (2) \\ &= 2\pi A F_1(r) dr dS \int_0^1 e^{-\lambda_1 r x} x dx \\ &= \frac{2\pi A dS}{\lambda_1^2} \cdot \frac{F_1(r)}{r^2} dr [1 - (1 + \lambda_1 r) e^{-\lambda_1 r}]. \quad (3) \end{aligned}$$

Also $dT = T_0 F_2'(r) dr. \quad (4)$

Thus $\frac{\partial N}{\partial T} = \frac{2\pi A dS}{\lambda_1^2 T_0} \frac{1}{r^2} \frac{F_1(r)}{F_2'(r)} [1 - (1 + \lambda_1 r) e^{-\lambda_1 r}]. \quad (5)$

The values of T which make N a maximum are given by $\frac{\partial N}{\partial T} = 0$, or

$$e^{-\lambda_1 r} = (1 + \lambda_1 r)^{-1}. \quad (6)$$

On this view T is determined by r alone, and the corresponding values of T are given by solving (6) for r and substituting in (1). The maximum value of the kinetic energy of the emitted electrons is that which corresponds to $r=0$, so that when $r=0$

$$\left(\frac{\partial N}{\partial T}\right)_{r=0} = \frac{\pi A dS}{T_0 F_2'(0)}. \quad (7)$$

Thus when T has its maximum value, $\frac{\partial N}{\partial T}$ has a finite value which is negative, since $F_2'(0)$ is negative. The value of $\frac{\partial N}{\partial T}$ when $T=0$ may be obtained by solving the equation $F_2(r)=P/T_0$ for r and substituting in (5). This value of $\frac{\partial N}{\partial T}$ is readily seen to be positive and finite, so that it is clear that the type of theory which supposes the maximum energy of the emitted electrons to be determined by the energy they receive under the influence of the light less a constant amount of work necessary for them to escape from the material is in satisfactory general agreement with the experimental results.

We shall not consider the numerical analysis of curves like those in fig. 3 in the present paper, but shall now turn to the experimental data which have been given by the other metals investigated.

Experiments with Different Metals.

Curves similar to those in fig. 2 were obtained by the same method for strips S of copper, bismuth, tin, zinc, aluminium, and magnesium, as well as platinum, using various wave-lengths of light. The curves for aluminium are represented by the full lines in fig. 2 (Pl. XIII.). The results with the other metals are shown in figs. 4, 5, 6, 7, and 8.

In each of these cases the curves for different wave-lengths reach saturation at a common point. The dotted ordinate in each figure represents the actual position of the current axis according to the reading of the voltmeter V , and the point where the dotted line meets the volt-axis is the experimental position of zero volts. But when this position of zero volts is shifted so as to correct for the contact difference of potential between the silver bulb and the metal strip used, the current-axis is shifted so as to pass exactly through the saturation-point where the curves coincide. For instance, the contact-difference of potential between silver and zinc is just 1 volt. When this is corrected for by shifting the position of zero volts to the right a distance corresponding to 1 volt, it is seen that this point, which really corresponds to zero field acting on the electrons, exactly coincides with the position where the curves reach their common maximum. This correspondence between the contact-difference of potential and the shift necessary to place the ordinate of zero volts at the saturation-point is exact, so far as we have been able to determine, in every case except that of magnesium, fig. 4. But doubtless even here the discrepancy is only apparent.

The fact that the shift required for coincidence is only 1.15 volts instead of 1.4 volts, the true contact-difference of potential between silver and magnesium, is probably due to slight oxidation of the magnesium, whereby the actual contact difference was reduced to 1.15 volts. So here, too, the shift and the contact-difference of potential probably correspond.

This point is also significant because it disproves the emission of electrons with apparent negative velocities. Since the curves reach their maxima at the ordinate which corresponds to zero volts, all the electrons possess velocities greater than zero. The occurrence of electrons with apparent negative velocities, that is to say, of electrons which are only completely liberated when there is an external electric field to draw them away from the surface of the emitting metal, has usually been supposed, in order to account for the fact that the distribution of velocity curves have often been observed to cut the axis of zero volts before reaching their maxima. Such an intersection with the current-axis is probably due either to the neglect of the effect of the contact difference of potential on the position of zero volts, or to something which prevents some of the electrons from reaching the receiving electrode unaided. Such an effect might be due to a poor vacuum, to electron reflexion, to the obstruction offered by a wire screen used in the effort to prevent reflexion, or to some peculiarity in the shape of the apparatus. Fortunately the difficulty seems to have been avoided in the form of apparatus used in this investigation.

It is now easy to understand why the values of the kinetic energies of the emitted electrons which have been published differ so widely. If the uncorrected position (the dotted line) were to be taken for the origin, it is evident that the different metals would appear to emit electrons with practically equal maximum velocities for a given wave-length, although actually those emitted by the electropositive metals possess the highest velocities.

In the case of sodium we have not been able to obtain the complete curves showing the distribution of kinetic energy. On account of the rapid photoelectric fatigue exhibited by this substance, we have only been able to determine the value of the maximum kinetic energy corresponding to different frequencies. Different methods were tried to reduce or avoid photoelectric fatigue, but they were only very partially successful. In our first experiments we cut the sodium surface in an atmosphere of hydrogen, carefully dried and purified, in a separate vessel attached to the bulb D; so that

the sodium strip could be placed in position without coming into contact with the air. But with the best care, the surface of the sodium coated over so rapidly that it gave no photoelectric current whatever. The plan finally adopted was to place a little strip of sodium in position at S, heat the bulb so as to drive off layers of adhering gas, and keep it under the highest vacuum obtainable with the Gaede pump for about 24 hours. Then the pump connexion was sealed off, and the bulb was left with a tube of phosphorus pentoxide and one of coconut charcoal immersed in liquid air for several hours more. After this a rod turning in a ground-glass joint provided with a mercury trap was turned, thus winding up a wire which drew a piece of Gillette razor-blade along so as to leave a fresh surface exposed to the light.

Even with these precautions the photoelectric sensitiveness of the sodium fell off rapidly, decreasing from a deflexion of 3000 divisions per minute to about 50 per minute in the course of two hours and a half. If photoelectric fatigue is due, as seems most probable, to the chemical effects of the surrounding atmosphere, it is clear that very minute amounts of matter can produce very sensible effects of this kind. The vacuum was unquestionably quite good in these experiments. Before applying the liquid air the pressure recorded by the McLeod gauge varied from amounts which were too small to be estimated, up to about 0.00001 mm.

As has been stated, we were not able to take the observations sufficiently quickly to obtain the complete velocity distribution curves for sodium. However, the maximum reading of the voltmeter at which any deflexion could be detected was quite easy to find. Such points correspond to the feet of the curves in Pl. XIII. fig. 2. These points were obtained as soon as possible after the sodium had been shaved and while the photoelectric currents were large, so that they should be quite accurate. In this way the following values were obtained:—

Wave-length.....	43.6	36.6	31.3	25.4	21
Apparent energy in equivalent volts...	-1.9	-1.5	-1.0	-0.2	+0.5
True energy in equi- valent volts	0.6	1.0	1.5	2.3	3.0

The true values of the kinetic energy were obtained by taking the contact difference of potential between silver and sodium to be 2.5 volts. This determines the position of the maximum point in the curves like those in Pl. XIII. fig. 3.

Having thus obtained the two end points, an estimate of the mean energy can be obtained by assuming that the shape of the curves is the same as that of those given by other substances which terminate at the same points. This method was tested in a number of other cases, where all the data were known, and found to give results for the mean energy which agreed with the direct determinations. Moreover, in almost all of the very large number of cases tried the curves between the same terminal points were identical to within the limits of experimental error. The curve which showed the worst agreement with this rule is the aluminium curve for $\lambda=31.3$, which runs across from the platinum curve at $\lambda=23$ to that at $\lambda=25$. This is shown in Pl. XIII. fig. 2. It is to be remembered, however, that a wave-length $\lambda=31.3$ gives very small currents even with aluminium, so that the curves in this part of the diagram cannot be determined very accurately. The more typical behaviour is shown by the curves for the wave-length 21 for Pt and 25.4 for Al, which are almost identical throughout their course (Pl. XIII. fig. 2).

*The Maximum and Mean Energies. Comparison
with Theory.*

The maximum and mean energies of the electrons emitted under the influence of light of a given frequency are readily obtained from curves like those shown in Pl. XIII. fig. 3. The maximum energy T_m , expressed in equivalent volts, is clearly equal to the intercept on the voltage axis between the point of intersection of the curves with this axis and that of the true axis of zero volts. The mean energy in the same units T_r is equal to the area which is bounded on the left by the curve, on the right by the true axis of zero volts, and below by the voltage axis, divided by the maximum current. The values of the maximum energy in this way are collected together in the following table (p. 585).

Leaving out of account for the present certain possible sources of systematic error, which will be considered more fully below, and which are likely to affect both the determinations of the mean and of the maximum energy in almost equal proportions, we are inclined to place more reliance on the measurements of the mean than on those of the maximum values. In some cases the current-voltage curves (Pl. XIII. figs. 2 & 4-8) appear to approach the voltage axis quite gradually, so that the determination of the exact point of intersection is a very difficult matter. Our electrostatic arrangements were quite sensitive and worked very satisfactorily; but the currents in this region are extremely

Metal λ_0 .	λ .	T_m .	T_r .	λ/λ_0 .	Metal λ_0 .	λ .	T_m .	T_r .	λ/λ_0 .
Na 57.7	43.6	0.60	0.30	0.755	Zn 35.7	26.5	0.92	0.52	0.740
	36.6	1.00	0.50	0.635		25.3	1.25	0.625	0.713
	31.3	1.50	0.75	0.542		23.0	1.70	0.862	0.644
	25.4	2.30	1.15	0.440		21.0	2.03	1.06	0.590
	21.0	3.00	1.50	0.365					
Al 41.1	31.3	0.90	0.365	0.760	Sn 33.7	26.5	0.80	0.432	0.785
	27.5	1.30	0.60	0.670		25.4	1.10	0.520	0.750
	25.3	1.50	0.74	0.615		23.8	1.33	0.660	0.705
	23.0	1.90	0.965	0.560		22.0	1.73	0.810	0.650
	20.0	2.30	1.21	0.485	Bi 33.7	25.4	0.60	0.315	0.750
Mg 39.0	27.5	0.85	0.45	0.730		23.0	0.90	0.450	0.680
	26.4	1.02	0.585	0.705		21.0	1.15	0.587	0.620
	25.4	1.35	0.638	0.675	Cu 30.9	26.0	0.35	0.175	0.840
	23.0	1.80	0.85	0.612		25.4	0.48	0.230	0.820
Pt 29.1	25.0	0.51	0.266	0.870		23.0	0.73	0.335	0.745
	23.0	0.99	0.47	0.790		21.0	1.02	0.475	0.680
	21.0	1.45	0.713	0.720	20.0	1.25	0.550	0.645	

The unit for λ is $1 = 10^{-6}$ cm. T_m and T_r are expressed in equivalent volts.

small, and the maximum potential observed is necessarily that at which the photoelectric current is balanced by the minute back leakage which is unavoidable in an apparatus of this character, and which arises chiefly from the ionization of the air in the shielding tubes and the like. It is possible that our measurements of the maximum energy light of greater intensity, as the Heraeus quartz mercury lamp was chosen for its steadiness rather than on account of the intensity which it furnished. However, it is probable that the chief sources of error in experiments on photoelectric action arise from chemical effects at the surfaces investigated rather than from defects in the electrical and optical arrangements used.

When the foregoing values of T_m and T_r are plotted against the corresponding frequencies ν , the results for each metal exhibit a linear relation between the corresponding variables. Except in the case of copper and bismuth the lines are almost parallel to each other for all the metals. The frequencies ν_0 , and the corresponding wave-lengths λ_0 , which correspond to T_m and $T_r = 0$, are determined by the intersection of these lines with the frequency axis. Together with the constant k ,

which determines the slope of the individual curves, they are collected together in the following table:—

Metal.	Values from T_m .			Values from T_r .		
	ν_0 .	λ_0 .	k_m .	ν_0 .	λ_0 .	k_r .
Na	51.5	58.3	5.2	52	57.7	2.6
Al	63	47.7	4.3	73	41.1	2.6
Mg	78.5	38.2	5.2	80	37.5	2.55
Zn	80	37.6	5.1	84	35.7	2.8
Sn	83	36.2	4.9	89	33.7	2.75
Bi	91	33	3.55	89	33.7	1.9
Cu	100	30	3.8	97	30.9	1.65
Pt	104	28.8	5.85	103	29.1	2.8

The unit for λ_0 is $1 = 10^{-6}$ cm. and for k_m and k_r
 $1 = 10^{-27}$ erg sec.

The values of λ_0 given by the mean energy T_r are practically identical with those given by the maximum energy T_m except in the case of aluminium. When the two differ we are inclined to attach more weight to the values from T_r for the reasons already stated.

Some years ago Einstein* showed that it followed from the unitary theory of light that the maximum energy T_m of the electrons emitted under the influence of light should satisfy the equation

$$T_m = h\nu - P, \quad \dots \dots \dots (8)$$

where ν is the frequency of the light, h is Planck's constant, and P the work which the electrons have to do in order to escape from the material. One of the writers † has recently shown that T_m and T_r have to satisfy the equations:—

$$T_m = h\nu - w_0, \quad \dots \dots \dots (9)$$

$$T_r = s(h\nu - w_0) \quad \dots \dots \dots (10)$$

where w_0 is the latent heat of evaporation of the electrons, per electron, at the absolute zero of temperature, and s is a quantity which depends upon the reflexion of electrons at the surface of the material. The precise definition of s is as follows. Consider the surface in question to form part of an isolated system in thermal equilibrium. It will be continually

* *Ann. der Physik*, vol. xvii. p. 146 (1905).

† O. W. Richardson, *Phys. Rev.* vol. xxxiv. pp. 146, 384 (1912); *Phil. Mag.* vol. xxiii. p. 615 (1912); *Science*, vol. xxxvi. p. 57 (1912).

emitting and receiving electrons. Of the incident group some will be absorbed and others reflected. Let the proportion absorbed be α . Then the proportion reflected is $1-\alpha$. Some of the electrons in the group under consideration have greater speeds than others; so that as the proportion reflected out of any group having a given speed is a function of the speed, the proportion of the energy, in a mixed incident group, which is reflected, will be different from the proportion of the incident number which is reflected. Let β be the proportion of the energy of the group, incident in the state of thermal equilibrium, which is absorbed. Then $s = \beta/\alpha$. As the proportion of incident electrons absorbed is smaller the higher the speed, it follows that s is a positive quantity which is less than unity.

The deduction of formulæ (9) and (10) does not depend on the unitary theory of light except in so far as the unitary assumption may implicitly underlie Planck's radiation formula, or rather Wien's form

$$E(\nu\theta) = \frac{8\pi}{c^3} h\nu^3 e^{-\frac{h\nu}{R\theta}}, \quad \quad (11)$$

which is used instead, as a sufficient approximation.

If we put $w_0 = h\nu_0$ we have instead of (9) and (10)

$$T_m = h(\nu - \nu_0), \quad T_r = sh(\nu - \nu_0) \quad . . . \quad (12)$$

or, in wave-lengths, putting $c = \nu\lambda = \nu_0\lambda_0$

$$\lambda T_m = ch \left(1 - \frac{\lambda}{\lambda_0}\right), \quad \lambda T_r = sch \left(1 - \frac{\lambda}{\lambda_0}\right). \quad . \quad (13)$$

A more comprehensive test of these formulæ is afforded by Pl. XIII. fig. 9, which contains all the observations which we have made. The points corresponding to the different metals are indicated thus:—

Na●, Al○, Mg*, Zn▲, Sn+, Bi∧, Cu×, and Pt⊥.

The values of λ_0 which have been used in constructing the figure are those given by plotting T_r , the mean energy, against ν . The points near the lines OB and OC represent values of T_m and those near OD and OE values of T_r . OA is the theoretical line for $T_m = h(\nu - \nu_0)$ using the value of h given by radiation measurements, viz. $h = 6.55 \times 10^{-27}$ erg cm. Except in the case of copper and bismuth, all the values of T_m lie very near the line OB and all those of T_r very near the line OD. The slope of the line OB corresponds to $k_{\text{th}} = 5.4 \times 10^{-27}$ erg sec. instead of 6.55×10^{-27} erg sec.

It is thus about 20 per cent. less than the theoretical value. The slope of OD is almost exactly half of that of OB. The slope of OC is only about two thirds of that of OB, but the same relation holds between OE and OC as between OD and OB. It thus appears that s is very close to one half for all the metals investigated, even including copper and bismuth, for which the discrepancy between k_m and h is much greater than in the case of the other six metals.

The relation $T_r = sh(\nu - \nu_0)$ has only been shown theoretically to hold for the case of isotropic radiation, that is for incident radiation which is propagated with equal intensity in all directions, whereas all the values given are for light at approximately normal incidence. However, we made special experiments with platinum and aluminium to see whether rotating the strip S so as to change the angle of incidence of the light would make any alteration in the curves giving the distribution of kinetic energy. We were unable to detect any certain changes in the energy in this way, although the number of electrons emitted varied considerably. It would appear, therefore, that the difference in the distribution of energy among the electrons emitted by isotropic radiation and those emitted by radiation incident at a particular angle, is inappreciable or, at least, its determination is not a practical matter when the degree of precision which is at present attainable in experiments of this kind is taken into consideration.

The fact that all of the measured values of λT_m fall to the left of the line OA is perhaps not very surprising. Practically every source of experimental error tends to make the measured values of T_m too small. This would be the case, for example, if the surface of the strip were covered with a layer of photoelectrically inactive material such as the oxide of the metal or a layer of condensed gas or moisture; the effect of any slight leakage in the electrostatic system is also in the same direction. We are unable at present to urge any satisfactory reason why the metals copper and bismuth should appear to be in a class by themselves.

It is worth while remarking that the difference between the experimental and the theoretical relation of T_m to ν is what one would expect if there were a layer of photoelectrically inactive material at the surface of the strips which reduced the speed of the escaping electrons, provided the law of diminution of kinetic energy T with thickness x of material traversed were of the form

$$\delta T = -Tf(x)\delta x. \quad . \quad . \quad . \quad . \quad . \quad (14)$$

This makes the energy lost proportional to the initial energy for different wave-lengths, and the relation between the observed T_m and ν a linear one. The slope, measured by k_m , of the experimental line would then be less than that (h) of the theoretical line. The two lines would intersect at $T_m=0$. This is in accordance with the experimental results if the experimental values of ν_0 are really identical with the least frequencies which would cause any electrons to be emitted from a perfectly clean surface. It might be, however, that the true values of ν_0 would be less than those observed, on account of the slowest electrons being completely stopped by such a layer. In that case the relation between T and x would have to be of the form

$$T = T_0 f(x) - g(x), \quad (15)$$

when T_0 is the maximum initial energy.

There is at present, so far as we are aware, no experimental evidence bearing on the law of loss of energy with matter traversed for these slowly moving electrons, but Sir J. J. Thomson * has deduced a formula of type (14) with $f(x) = \text{constant}$, on theoretical grounds. The application of this formula can hardly be regarded as having much cogency in the present instance, but it is of some interest to see what it leads to, in the way of an estimate of the thickness of inactive matter required to produce the observed differences between theory and experiment. In the least favourable case, that of bismuth, assuming the inactive matter to be Bi_2O_3 , we find $x = 2.5 \times 10^{-4}$ cm. In the other cases the thickness would vary down to about one-tenth of this. Thicknesses of inactive matter of this magnitude should produce distinct optical effects. The only case in which we observed visible changes of this kind was that of copper, the surface of which became darker during the experiments. The existence of photoelectric fatigue shows that the surfaces of the metals do become covered with a layer of inactive matter. Tests which we have carried out show that the change in the maximum energy and in the distribution of energy of the emitted electrons due to photoelectric fatigue is uncertain, but is certainly inappreciable in comparison with the change in the number of electrons emitted. However, a layer of inactive matter might easily have the effect of reducing the number of escaping electrons very considerably without causing any comparable change in the distribution of velocity among those which got through, particularly as the mode of distribution is fairly irregular to start with. It is significant

* 'Conduction of Electricity through Gases,' 2nd edition, p. 379.

that the metals for which the values of k_m show the nearest approach to the theoretical value are platinum and sodium. The former is notoriously averse to oxidation and the surfaces of the latter were cut *in situ* in the best attainable vacuum.

The Values of ν_0 and λ_0 .

According to the theory which underlies formulæ (9) to (13)

$$w_0 = h\nu_0, \dots \dots \dots (16)$$

where w_0 is the latent heat of evaporation of electrons out of the material at the absolute zero of temperature. The value of w_0 can be obtained from thermoelectric data combined with the temperature variation of the rate of emission of electrons from the material when heated. The metal which has received the most extended study in this respect is platinum, and it is probable that a fairly reliable estimate of w_0 can be obtained for this material. If σ is the specific heat of electricity, one of the writers * has shown that

$$\sigma = \frac{1}{e} \left\{ \frac{R}{\gamma - 1} - \frac{\partial w}{\partial \theta} \right\}, \dots \dots \dots (17)$$

when e is the charge on an electron, R is the gas constant for one molecule, γ is the ratio of the two specific heats for the electrons, and w is their latent heat of evaporation, per electron, at temperature θ . According to Berg † the Thomson coefficient for platinum is practically constant between -50°C. and $+100^\circ \text{C.}$ and equal to -9.2×10^2 erg per E.M.U. per $^\circ \text{C.}$ Thus from (17) w is a linear function of θ . If n is the total number of electrons emitted thermionically at θ , when the coefficient of reflexion of the electrons is neglected

$$n = A_1 \theta^{\frac{1}{2}} e \int \frac{w}{R\theta^2} d\theta, \dots \dots \dots (18)$$

where A_1 is independent of θ . Substituting the experimental numbers given by the Thomson effect, this becomes

$$n = A_2 \theta^{2.11} e^{-w_0/R\theta}, \dots \dots \dots (19)$$

where A_2 is independent of θ and w_0 is the value of w when $\theta = 0$.

We have applied the formula to determine w_0 from the experimental measurements of the saturation electronic

* O. W. Richardson, *Phil. Mag.* vol. xxiii. p. 605 (1912).

† Cf. Baedeker, *Elektrische Erscheinungen in Metallischen Leitern*, p. 76.

currents from platinum at different temperatures, which have been made by F. Deininger *, H. A. Wilson †, and O. W. Richardson ‡. These are probably the most reliable determinations which have been made, and although they are not in perfect agreement there is no reason why any one of them should be rejected. The values of w_0 in equivalent volts calculated in this way are :—Deininger, 5.03; Wilson, 5.39; Richardson, 5.61. The mean is 5.34 volts or 8.32×10^{-12} erg using $e = 4.67 \times 10^{-10}$ E.S.U. The value of ν_0 for platinum in the table on p. 586 is 1.03×10^{15} sec.⁻¹ whence

$$h = w_0/\nu_0 = 8.07 \times 10^{-27} \text{ erg sec.} \quad . \quad . \quad . \quad (20)$$

It will be observed that this estimate of h depends only on thermionic, thermoelectric, and photoelectric measurements, and is quite independent of the estimate $k_m = 5.85 \times 10^{-27}$ erg sec. Nevertheless it is very close to the radiation value $h = 6.55 \times 10^{-27}$ erg sec. The value (20) is, in fact, just about as much in excess of the radiation value as the other is below it.

The discrepancy between the value of h from w_0/ν_0 and from the radiation formula might be due either to w_0 being too large or ν_0 being too small. It is possible that the values of ν_0 estimated from the linear relation between T and ν are too small for some unknown reason; but it is not possible that they are sufficiently in error to account for the whole of the discrepancy. This is shown by the fact that in the case of platinum the photoelectric emission was definitely measurable at $\lambda = 27$ as compared with the value $\lambda = 29.1$ deduced from the measurement of T_r . There is therefore only a possibility of an extension of λ_0 of about 2 units in this direction, and this would only account at most for about half the observed difference. As a matter of fact the tabulated values of λ_0 on p. 586, although rather higher than the wave-lengths at which photoelectric emission was observed to start, were never very far from them. Although we have made experiments in this direction with most of the substances investigated, we have not been able to satisfy ourselves that there is any certain difference between the tabulated values of λ_0 and the greatest wave-length at which photoelectric emission commences. The tests made, however, are not as delicate or reliable as might be desired, on account of the photoelectric insensitiveness of the materials in this

* *Ann. der Physik*, vol. xxv. p. 296 (1908).

† *Phil. Trans. A*, vol. cci. p. 243 (1903).

‡ *Phil. Trans. A*, vol. ccvii. p. xxiii. (1906).

region and of the fact that our source of light gave a line spectrum.

It seems, therefore, fairly certain that part of the increased value of h deduced from (20) must be due to w_0 being too large. We think it improbable that w_0 is appreciably larger than what it pretends to be, namely, the part of the latent heat of evaporation of the thermionically emitted electrons which is independent of θ . It may be, however, that w_0 is slightly smaller for the electrons emitted photoelectrically by the complete radiation, than it is for the electrons which are emitted thermionically. If this could be established it would be important as showing that thermionic emission is something different from the photoelectric emission arising from the complete radiation characteristic of the temperature of the hot body*.

The values of ν_0 for different substances are closely related to the contact differences of potential. This is shown by the numbers in the following table, which represent the contact differences of potential between platinum and the different metals investigated:—

Metal. I.	Contact P.D. with Platinum. (Volts.)		
	Calculated. II.	Observed. III.	Calculated. IV.
Cu	·37	·13	·30
Bi	·77	·35	·64
Sn	·77	·62	·64
Zn	1·04	·90	·85
Mg	1·17	1·05	1·00
Al	1·62	1·2	1·31
Na	2·69	2·4	2·2

The observed values in column III. are the usual values, except in the case of Mg, where the observed value was ·25 volt less than that given in the standard tables. The calculated values in columns II. and IV. are derived from the corresponding values of w_0 in different ways. The differences of w_0 are taken to be equal to the differences of eV , where V is the corresponding intrinsic potential. This is in accordance with the formula

$$w_m - w_p = e(V_m - V_p - \theta \frac{\partial}{\partial \theta} (V_m - V_p)), \quad . \quad . \quad (21)$$

* Cf. O. W. Richardson, Phil. Mag. vol. xxiii. p. 620 (1912).

since the term involving θ , which depends on the thermo-electric power of the metals, may be disregarded in the cases considered on account of its smallness. For similar reasons the differences of w may be taken to be the same thing as the differences of w_0 .

The values in column II. were obtained by assuming that the value of w_0 for platinum was equal to that given by the thermionic measurements, viz. 5.34, in equivalent volts. A factor A was then determined so that $h\nu_0 = A \times 5.34$ where $h = 6.55 \times 10^{-27}$ erg sec. and $\nu_0 = 1.03 \times 10^{15}$ sec.⁻¹ the value of ν_0 for platinum given by the experiments. This value of A was then used as a reduction factor to determine the value of w_0 from that of $h\nu_0$ for each of the other metals. This method is equivalent to assuming that the value of w_0 is the same for the photoelectric as for the thermionic emission, and that the large value of h given by (20) is due to some unknown error in $h\nu_0$ which affects the different metals proportionately.

The values in column IV. are simply the differences of $h\nu_0$ reduced to volts per unit charge. This method of calculation is equivalent to assuming either that w_0 is in error or that it is not the same thing for photoelectric as for thermionic emission. All things considered, both II. and IV. give a fair agreement with III., although the last column agrees better than the second. On the whole, the view which puts the error in (20) on w_0 has, so far, the best of the argument.

The Frequency of Characteristic Röntgen Rays.

If the formula $T_m = \nu h - w_0$ continues to apply no matter how high the frequency ν becomes, the frequency of characteristic Röntgen rays can be written down from known data. There is nothing in any derivation of the formula which would tend to confine its application to any limited range of frequency. On the other hand, its validity is closely connected with that of Planck's radiation formula, which has only been tested in the neighbourhood of the visible spectrum. The extension to the case of Röntgen rays can therefore only be regarded as speculative; as a speculation however, it has some merit, since it is the only line of attack which seems open to us at present.

The researches of Sadler* and Beattie† have shown that when characteristic Röntgen rays fall on different substances, the energy of the emitted electrons is independent of the substance emitting them, being determined entirely by the

* Phil. Mag. vol. xix. p. 337 (1910).

† Phil. Mag. vol. xx. p. 320 (1910).

character of the X rays. Whiddington* has shown that the maximum energy of the emitted electrons is equal to that of the slowest cathode rays which will excite the characteristic Röntgen rays. He has measured this quantity in equivalent volts in a number of cases and has shown that, in general, for Barkla's K series of X rays the energy is proportional to the square of the atomic weight of the metal of which they are characteristic. These results are consistent with the formula $T_m = h\nu_0 - w_0$ for the energy of the emitted electrons provided ν_0 , the frequency of the characteristic Röntgen rays, is given by

$$\nu_0 = 6.55 \times M^2 \times 10^{14}, \dots \dots \dots (22)$$

where M is the atomic weight of the metal of which they are characteristic. This holds only for the rays which constitute Barkla's K series. The values for the L series should be given by substituting $\left(\frac{M}{2} - 25\right)$ for M in (22), to accord with Whiddington's conclusions. Thus the frequency of the Röntgen rays characteristic of copper would be, since they belong to the K series,

$$\nu_0 = 2.64 \times 10^{18} \text{ sec.}^{-1}.$$

In the case of all these rays w_0 is negligible in comparison with $h\nu_0$. This accounts for the energy being independent of the metal of origin, as found by Sadler.

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LIV. *The γ Rays excited by the β Rays of Radium.*
By J. CHADWICK, M.Sc.†

IT has been shown by Gray‡ that when the β rays of radium E impinge on any material they excite γ rays. The amount of the excited γ rays is large compared with the amount of primary γ rays. He has found that the excited γ rays increase in amount and in penetrating power with the atomic weight of the material on which the β rays impinge.

* Roy. Soc. Proc. A. vol. lxxxv. p. 323 (1911); vol. lxxxvi. pp. 360, 370 (1912).

† Communicated by Prof. E. Rutherford, F.R.S.

‡ J. A. Gray, Proc. Roy. Soc. A. vol. lxxxv. p. 131, and vol. lxxxvi. p. 513.

FIG. 3.

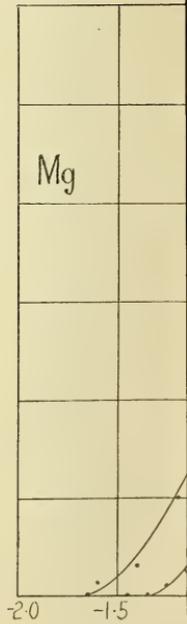
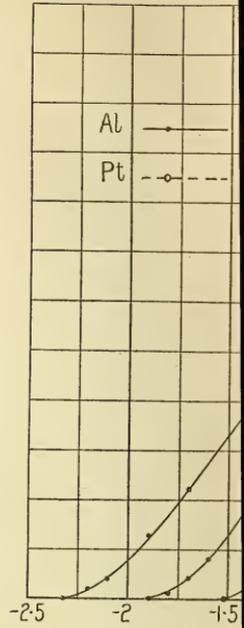
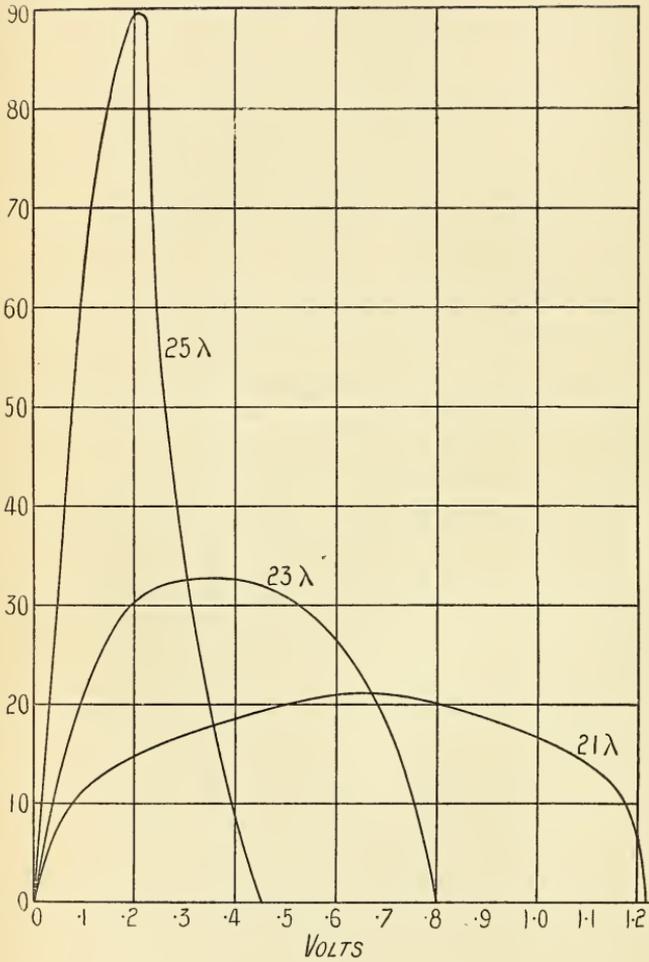


FIG. 2.



FIG. 4.

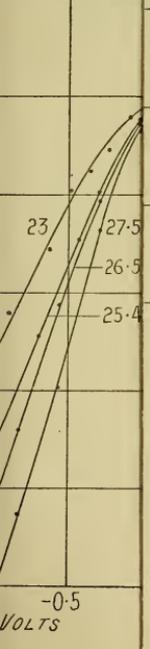


FIG. 9.

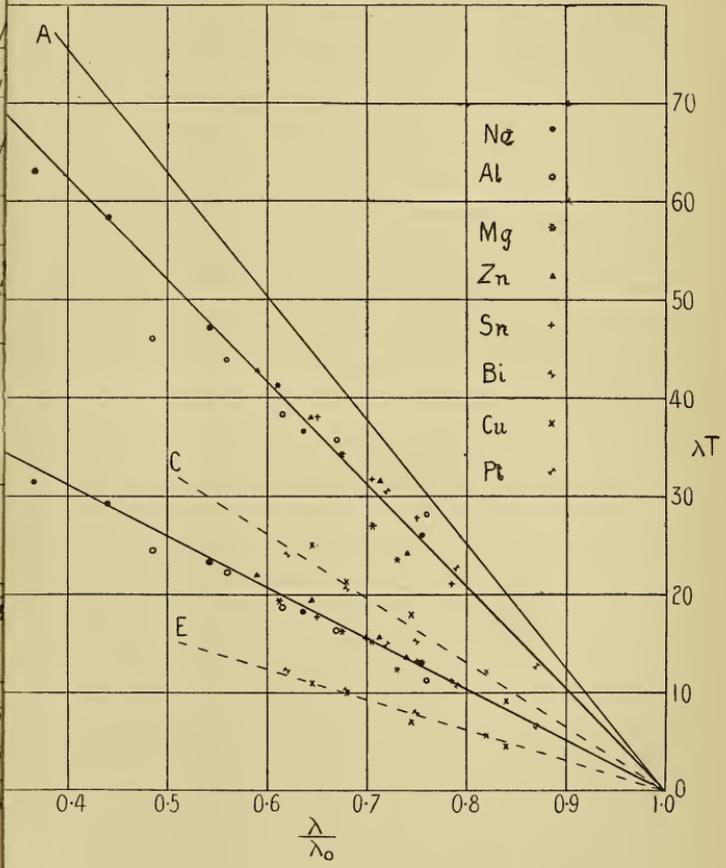


FIG. 3.

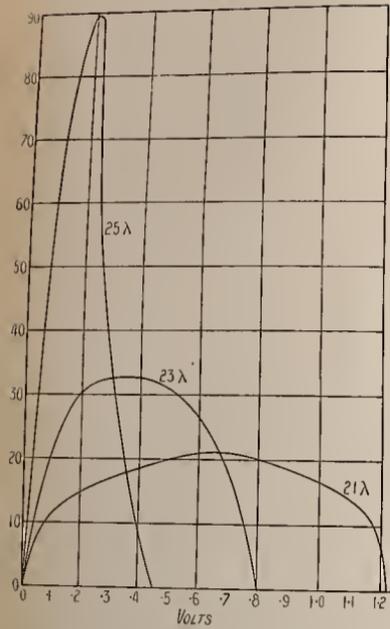


FIG. 2.

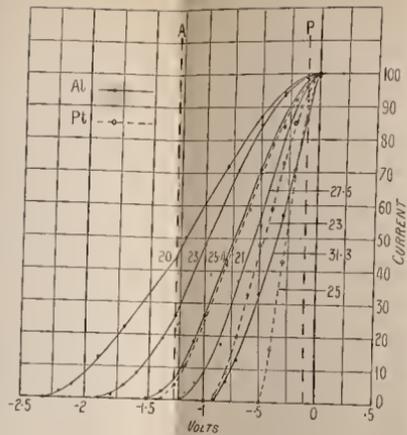


FIG. 4.

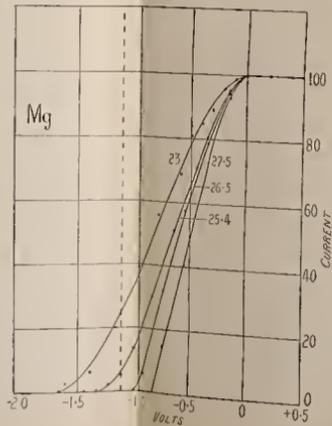


FIG. 5.

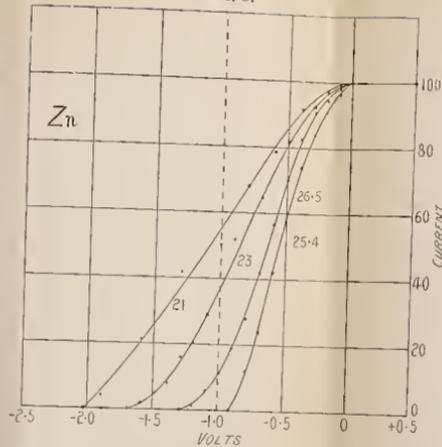


FIG. 6.

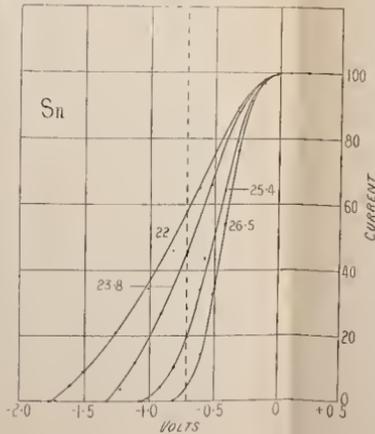


FIG. 7.

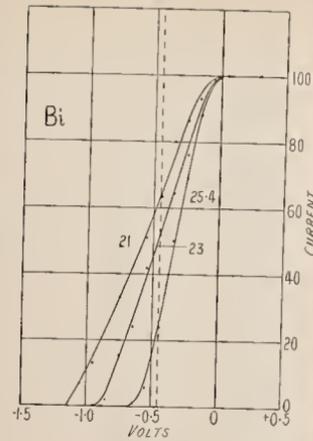


FIG. 8.

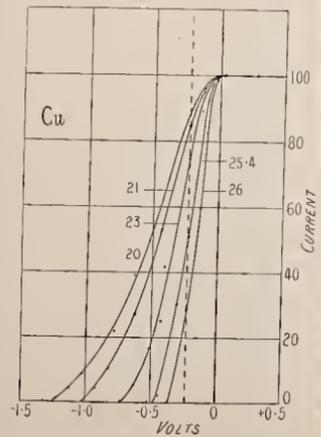


FIG. 9.

