THE EMISSION AND ABSORPTION OF PHOTOELECTRONS BY PLATINUM AND SILVER.[1]

By Otto Stuhlman, Jr.

As the result of light passing through very thin metal foil, photoelectrons will be emitted from both sides of the metal simultaneously. Since it will be necessary to distinguish between those electrons which are liberated from the side upon which the light is incident and those that come from the side from which the light emerges, we shall refer to them as "incidence" and "emergence" rays respectively.

It was hoped that some relations could be established between the atomic properties of metals and their photoelectric emissivity. Secondly to establish the magnitude of the coefficient of absorption of the electrons as a function of their speed and atomic properties of the metal in which the absorption was to take place. Finally to use the above information, if adequate, to throw some light on the structure of the atom.

All previous work by the writer and other investigators[2] who have been interested in the photoelectric properties of very thin metallic foil, or still thinner and transparent films of metal was undertaken with cathode deposited films supported by quartz.

The photoelectric currents and velocity investigations were, however, found to depend too much upon the previous history of the cathode and the potential gradient under which the cathodic deposit had been made to warrant any quantitative conclusions.

Thus in many cases, as in those investigations by the writer and K. T. Compton, both the magnitude of the current and the velocity of emission of the electrons could be altered at will, depending upon the impurities that are present through occlusion, in the cathode. The most serious difficulty, however, was found in mounting the very thin transparent films in such a way as to insure perfect electrical contact. These sources of error were so great that no quantitative conclusions could be drawn from the data at that time.

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[1] Presented at the Amer. Phys. Soc. meeting, December 27, 1917.

[2] Stuhlman, Phil. Mag., 20, p. 331, 1910; 22, p. 854, 1911; Phys. Rev., 4, p. 195, 1914. Stuhlman and Compton, Phys. Rev., 2, Sept., 1913. Kleeman, Proc. Roy. Soc., 84, p. 92. 1910. Robinson, Phil. Mag., 23, p. 542, 1912; p. 115, 1913; V., 32, p. 421, 1916. Werner, Ark. Mat. Ast. Fys., 8, No. 27, p. 1, 1913. Partzsh and Hallwachs, Annalen XLI., p. 247, 1913. Compton and Ross, Phys. Rev., 9, p. 559, 1917.

In the present work it was found necessary to investigate metallic films of less than 10^{-6} cm. in thickness with a degree of accuracy much beyond that heretofore attained in the above experiments. It was necessary to provide films of extreme purity and make electrical contact with them which would exclude the errors introduced through direct contact clamping between these very thin films and their supports leading to the electrometer. Heretofore successive thicknesses of films were produced either through successive additions of metal to an initial thin film, or successive plates were covered with various thicknesses and then separately investigated. This necessitated the investigation of many films of varying thickness deposited on the assumption that a linear relation existed between time of sputtering, and thickness of metal deposited. To attain this experimental linear relation by keeping the working conditions constant enough in the cathode-depositing-chamber through control of vacuum and cathode fall is itself quite a difficult undertaking.

TRANSPARENT METALLIC WEDGES WERE DEPOSITED.

In order to obviate the necessity of examining a large number of transparent films of successive increasing thickness, or of examining one film which had been built up of successive layers which had been photoelectrically fatigued through long use, the feasibility of substituting a transparent or semi-transparent metallic wedge was considered.

The deposition of such a wedge by an electrolytic method was however rejected. The difficulties of this method of deposition may be appreciated since we learn from Kundt's[1] well-known experiments on the optical constants of metals, that out of several thousand attempts only a score of wedges were produced which were sufficiently perfect to warrant investigation. A further objection however arises. A chemically deposited metal would contain impurities through occlusion of the electrolyte with the subsequent formation of polarized electrical double layers, which may become so prominent as to prevent all electronic emission.

A metallic wedge deposited by evaporation in vacuo from a fine wire, heated to luminescence, was eventually found to meet the above requirements and objections.

The method[2] essentially consists of a wire, heated to incandescence by means of an electric current, while the quartz plate upon which the wedge is to be deposited is placed below and to one side of it. If the whole is now placed in vacuo, the metal will vaporize and condense upon the quartz surface and surrounding objects.

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[1] See Kayser Handbuch der Spectroscopie, IV. Band. p. 542.

[2] Stuhlman. Presented before the Amer. Phys. Soc., New York meeting, December, 1916. Also Jour. Optical Soc. of Amer., V., 1, p. 78, 1917.

Under similar conditions Langmuir[1] has shown that the rate of evaporation m of an incandescent body is expressed by the relation

$$m = \sqrt{\frac{M}{2\pi RT}} \cdot p,$$

where M is the molecular weight of the vapor and p its vapor pressure. He has also shown that no reflection of molecules of the metal takes place at the surface upon which they initially strike, unless the surface is so hot as to cause reëvaporation. Under the above conditions we can therefore conclude that the total amount condensed per second is equal to the loss per second which the wire undergoes through evaporation.

Hence given a wire whose cross-sectional area is small compared with its distance above the plane, over which it is placed horizontally, it may be treated as a linear source which is sending out metallic vapor in all directions at right angles to its surface. Since no reflection takes place from the horizontal plane under the working conditions, then $dm/2\pi$ can represent the amount of evaporated metal passing through unit angle per second and subsequently condensed from a length dl of wire. Let the wire be stretched parallel to and at a height h cm. above the horizontal plane in which the quartz plate is placed, upon which the deposition is to form. After n seconds let t_0 represent the thickness of the metal condensed on the plane just below the wire. The flux per second of metal through an angle $d\theta$ condensing just below the wire producing this thickness t_0 is then

$$t_0 h d\theta = \frac{dm}{2\pi} d\theta.$$

The simultaneous condensation at any other point in the plane at a perpendicular distance r from the wire is given by

$$t_n ds = \frac{dm}{2\pi} d\theta.$$

Since

$$t_0 h d\theta = t_n ds = \frac{t_n r d\theta}{\cos\theta}$$

it follows that the thickness of deposit at any point in the plane is

$$t_n = \frac{t_0 h^2}{h^2 + x^2}, \qquad (1)$$

where x represents the distance of the point n from the foot of the perpendicular h let fall from the wire to the plane. If we set $h = 2a$ and $t_n = y$ the equation reduces to the well-known curve

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[1] Phys. Rev., V., 2, p. 340, 1913.

$$y = \frac{8a^3}{x^2 + 4a^2}, \tag{2}$$

the "Witch of Agnesi," so that a section through the solid deposit formed from an evaporating wire, at constant temperature, with vacuum at constant pressure can be represented by the above curve. The deposit just below the wire is however not a wedge. It has a pronounced curvature concave downward, followed by a curvature concave upward. Further along, that is for the values of x ten times larger than values of y, the curve approaches a straight line. It was in this region that the quartz plate was placed, which was to receive the metal, where the deposit would approach nearest to the desired form of a true wedge.

APPARATUS USED TO DEPOSIT WEDGES.

Fig. 1 shows a diagrammatic representation of the apparatus. Although originally[1] designed to make interferometer or opaque mirrors of uniform texture and optical purity, it was found to answer the requirements for the present purpose. The working parts are mounted on a thick plate of rolled brass, grooved to hold the bell jar *BJ*. Hard sealing wax floated in this groove formed the seal for the vacuum which was maintained by means of a Gaede rotary mercury pump. The carriage *HE* supports the incandescent wire. At *H* the wire is attached to a screw at the top of the rod connecting the two wheels, from where it passes down and then through a large hole in the rod between the wheels, then across through a similar hole in the rod at *E*, thence to the spring brass hook, *E*. This spring hook supplies the necessary tension to the wire. Upon heating the wire, it expands and the slack is further taken up by the spring in the hook. For the heating current a 110-volt alternating current was used. The quartz plate was placed in the plane *P* below and to one side of the wire.

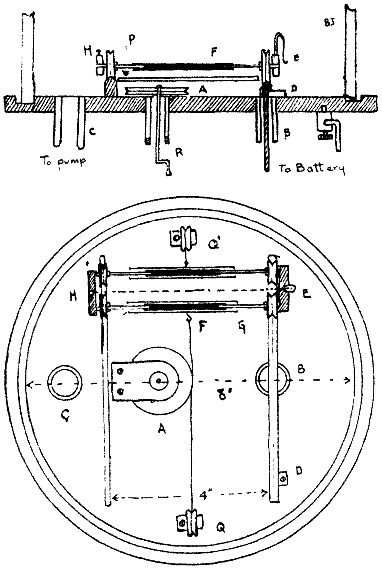

Fig. 1.

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[1] Read as a paper before the Amer. Phys. Soc., New York, December, 1916. Jour. Optical Soc., V., 1, p. 78, 1917.

The heating-current enters the base plate at the binding post to the right. It then passes into the metallic track at H which is screwed to the base plate. From here it passes through the left side of the carriage, thence through the wire across to E into the right-hand track. This track is insulated from the base-plate by means of two fiber L-shaped supports. The current passes from this insulated track through the rod B back to the battery. The rod B passes through a hole in the base-plate and is sealed in place with hard red sealing wax, which serves to insulate it from the plate and at the same time makes the opening air tight.

To prevent the carriage supports from short circuiting the glowing wire, they are separated by hard fiber rods. This joint F was then covered with a tight-fitting glass tube extending one centimeter beyond each end of the fiber insulation. This prevented the fiber from being coated with a metallic deposit which would otherwise short circuit the glowing wire. In order to shift the carriage it was necessary to have a mechanical control outside of the apparatus. (A magnetic control would be simpler for the present purpose.) It was supplied by means of a small crank which passed through a ground glass stopper sealed in the tube at R. This crank turned the horizontal V-grooved wheel A, around which passed a belt to the small wheel Q, from where it passed to a hook on the carriage at F. The other end of the belt passed over a similar wheel at Q' and thence to a similar hook on the other side of the carriage. By turning the crank R, the carriage and wire could be rolled to any position above the plane P which contained the quartz plate upon which the metallic wedge is deposited.

In order to insure a very pure deposit it was found necessary to acid clean the wire thoroughly. It was then mounted and heated in vacuo, but not so high as to produce evaporation. This removed most of the occluded gases and such impurities which would otherwise have been condensed on the quartz plate. The wire is now set at the proper distance from the quartz plate and allowed to vaporize until the desired thickness of metal has been attained.

A metallic deposit condensed as outlined above, was first examined for change in thickness as the distance from the wire increased; with a view of ascertaining how near photometric measurements could determine changes in thickness. A glass microscope slide 10 × 1 cm. was placed directly beneath and 1 cm. below the wire and the metal was deposited until the region just below the wire was opaque. The deposit was next examined by means of a microphotometer with unresolved light from a tungsten filament lamp. A beam 1 × 10 mm. was directed normally on the metallic side and after passing through the wedge was focussed on a linear thermopile in vacuo. The throw of a ballistic galvanometer in series was used to measure the current, which was assumed to indicate, in a rough way, the change in thickness of the wedge as successive millimeter portions were passed before the slit of the thermopile.[1] No quantitative conclusions were expected from these data due to the change in the optical constants with change in thickness of the film.

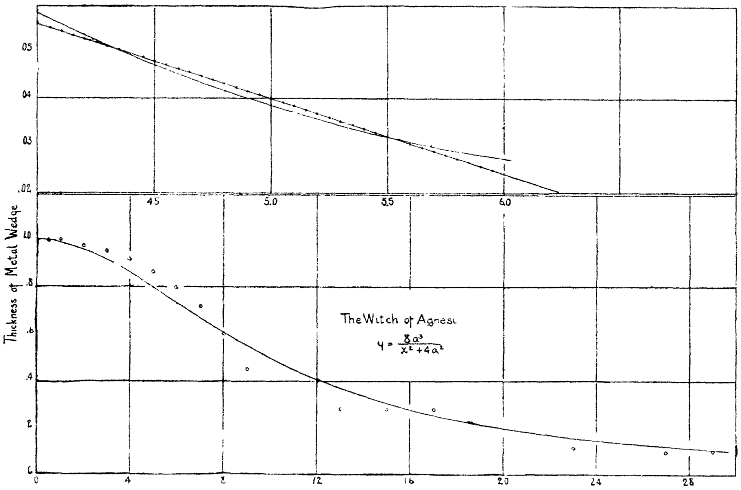

Fig. 2.

These more or less approximate results are shown in the lower curve of Fig. 2. The agreement between the observations as recorded and the theoretical equation $y = 8a^3/(x^2 + 4a^2)$ plotted, as a full line, are as close as might be expected under the circumstances.

In order to determine how near to the wire the best approach to a true wedge could be expected, the following graphical method was resorted to. The theoretical curve was plotted on large scale coördinate paper and that part of the curve chosen which fitted nearest to a straight line within an average of five per cent. The upper graph in Fig. 2 shows the portion of the curve chosen. The solid line represents values computed from the theoretical equation, for the thick end of the wedge at a distance of four centimeters from the foot of the normal let fall from the wire to the plane. The broken graph is a straight line drawn through the average value of the points. Although the metal deposited at this distance from the wire has a slightly concave surface, yet it approaches a straight

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[1] I am indebted to Dr. Ives, of the United Gas Improvement Co., Philadelphia, for the use of this apparatus, and to Dr. Eckhardt for assistance with these observations.

line wedge with not more than a maximum of five per cent. variation at any point. This five per cent. error, contributed by the straight line assumption, is within the error of observation contributed by the subsequent photoelectric current measurements.

The metallic wedges investigated in this paper were all deposited in this region.

The Wedges.

The metals investigated were platinum and silver. They were deposited from chemically pure wires .043 cm. in diameter. The wire was 12 cm. above the plane which contained a 2.5 × 1.0 × 0.1 cm. quartz plate placed four centimeters away from, with its narrow side parallel to, the incandescent wire.

The platinum wedges, when examined by reflected light, showed for the opaque deposit at the edge nearest to the glowing wire, the characteristic metallic lustre of the metal. Semi-opaque thicknesses transmitted red light and reflected blue. As the thickness decreased the reflected light changed from blue to brown, to yellow, to blue and at the very thinnest end to indigo. The colors of the transmitted light for the same thicknesses were gray brown, greenish blue and reddish brown.

Silver wedges which were opaque at one end and shaded to zero thickness at the other end in 4 cm. of length showed the following variation in color. Deep violet was transmitted through the nearly opaque thicker end, shading into violet, blue, light blue, deep blue, purple, red, brown and into yellow at its thinnest end. The corresponding points when viewed by reflected light showed at the opaque end the metallic luster of silver followed by deep green, green, green blue, red green, red, blue red, blue and a lighter blue at its thinnest end.

An absorption band might hence be expected to exist in the green part of the spectrum about λ 4500. An absorption spectrum photograph obtained by means of a Hilger monochromatic illuminator through one of the silver wedges, showed a continuous gradually increasing absorption through the red and yellow, terminating at about λ 5300, from here a weak broad green blue absorption band exists terminating at about λ 4000 from where the absorption again drops off regularly into the violet but at a greater rate than the ascent in the red end.

While the thick and nearly opaque ends of some of the platinum wedges are transparent to red light (in fact the glowing filament of a tungsten lamp was visible through the thick end as a brilliant red image); the thick or nearly opaque end of the silver wedge showed the same filament as an indigo-blue image. Showing that the shorter wave-lengths penetrate further into a silver surface than into platinum. What evidence the photoelectric observations throw on this topic will be discussed in a separate chapter.

The Arrangement of the Apparatus.

The metallic wedge (1 × 2.5 cm.) supported by the quartz plate is shown in Fig. 3 as *Q*. It was mounted with the thick end of the wedge attached to the brass holder *E*. A countersunk screw pressed the metal-covered side of the quartz plate rigidly against the opposite facet of the clamp at *E*. This clamp was screwed to a rod ending in a rack *B*, which slid under V-shaped grooves in the fixture *A*. The pinion *N* engaging the rack, pushed the wedge into any desired position with respect to the beam of light *T* which was used to excite the photoelectric phenomena. The position with respect to the illumination was indicated on the steel millimeter scale *S* fastened to the fixture at *A*. This motion of the wedge allowed one to expose successively increasing or decreasing thickness of the metal to the beam of ultra-violet monochromatic illumination passing through a Hilger Monochromatic Illuminator placed in front of the slit *R*. A 110-volt Cooper Hewitt quartz mercury arc running under constant power supplied the illumination. The slit at *R* was so adjusted that a clear cut image 8 mm. long and 0.23 mm. wide fell on the quartz plate at *T*. The degree of sharpness of the image and its position was at all times controlled by means of a fluorescent plate which could be substituted for *Q* and by means of a fluoroscope eye piece placed at *O*. The photoelectric chamber *D* is an oxidized copper cylinder covered with camphor soot whose photoelectric constants were well known, having been repeatedly used in former experiments. This cylinder D was mounted coaxially with the outer brass casing *P*. It was connected as shown, to an electrometer after passing through the hard sealing wax support at *P*. The electrometer showed a consistent sensibility of 1,220 divisions per volt which did not vary more than 1.3 per cent. during the course of the experiments.

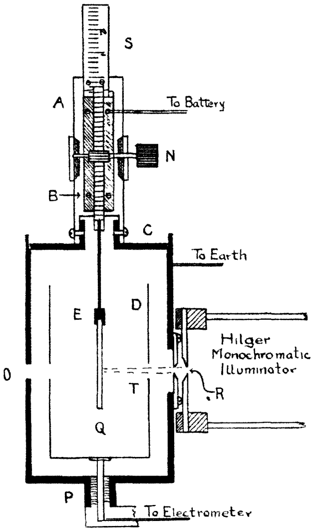

Fig. 3.

The present method differs fundamentally from previous measurements on thin metal films in so far as photoelectric current can be measured from one film, possessing various thicknesses and having the same history of production and ageing. An additional improvement consists in being able to examine the very thinnest film without introducing special appliances or precautions for electrical contact. It also allows one to measure the thickness of the very thin films to a greater degree of accuracy through extrapolation from the thicker films, which in turn lend themselves more easily to accurate measurements.

The wedge was exposed at millimeter intervals through its entire length. The present paper deals with the photoelectric current obtained from such a wedge when the metal side faced away from the light. Under these conditions the illumination was allowed to fall under normal incidence on the quartz side of the plate, it then passed through the transition layer quartz-metal and liberated photoelectrons in the metal. The electrons leaving the metal under these conditions are classified as "emergence." To measure the "incidence" effect all that was necessary was to rotate the superstructure in the groove *C* through 180° and repeat the measurements for thicknesses as relatively determined by the scale *S*.

Film Thickness.

The determination of the thickness of the film contributed the largest error to the final results. Optical methods as developed by Wiener[1] were given up as too unreliable. A very promising method, though not used on the data presented below, and especially adaptable to silver films, is that in which the silver film is locally converted into silver iodide by means of the proximity of a minute piece of iodine. A convex lens placed upon the resulting hump allows one to use the Newtonian ring interference method for computing the thickness of the hump and from it a value of the thickness of the original silver.

Here either mechanical or electrical methods were resorted to. As in the case of platinum, when the specific resistance of the material is known in terms of thickness,[2] it was found feasible to determine the thickness at several points along the wedge by using the following indirect method.

A quartz plate, similar in size to the one upon which a wedge was deposited, was covered with a uniform film, of thickness comparable to the thick end of the wedges. This uniform film can be deposited in the apparatus discussed above by simply moving the carriage, supporting the incandescent wire, back and forth across the plate with uniform speed. After attaining its equilibrium value the film was examined for its spe-

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[1] Wied. Annalen, V., 31, p. 629, 1887.

[2] Patterson, Phil. Mag., IV., p. 663, 1902. Longden, Phys. Rev., II., p. 40, 1900. I. Stone, Phys. Rev., VI., p. 1, 1898.

cific resistance. This resistance data could be used to compute its thickness. A photoelectric examination of this uniform surface made under similar conditions as existed when the wedge was investigated, determined the thickness of that part of the wedge which showed an equal photoelectric current.

When the thickness of the plane film was large enough, the above method was checked by direct weighing. The plane silver films could be changed to the iodide form, and then weighed, and from these results the thickness can be computed.[1]

EMERGENCE PHOTOELECTRIC CURRENT OBSERVATIONS.

The photoelectric currents for wave-lengths 2260, 2301, 2536 and 3131 were obtained for platinum and silver with variations in thickness of the metal exposed. Since the various spectral lines are not of equal intensity the observations were reduced to represent current per unit incident light intensity, by dividing the number of electrons liberated per unit time by the energy of the light of the corresponding wave-length.

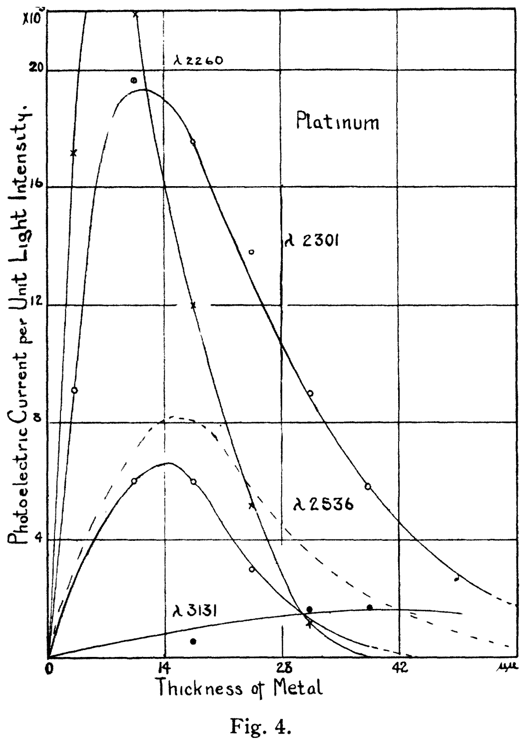

Fig. 4.

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[1] Quinicke, Pogg. Ann., 129, p. 178, 186 .

The ordinates thus plotted in subsequent curves represent the relative number of electrons liberated in unit time by a unit amount of light-energy for the wave-length indicated.

In the case of platinum an attempt was made to get some results from λ 3131 but with little success, since platinum is no longer photoelectric sensitive for this wave-length. These latter results are only introduced for qualitative comparison, and since no light filter was used, no doubt the observed current was not really due to the excitation from this wave length, but from a somewhat shorter wave-length.

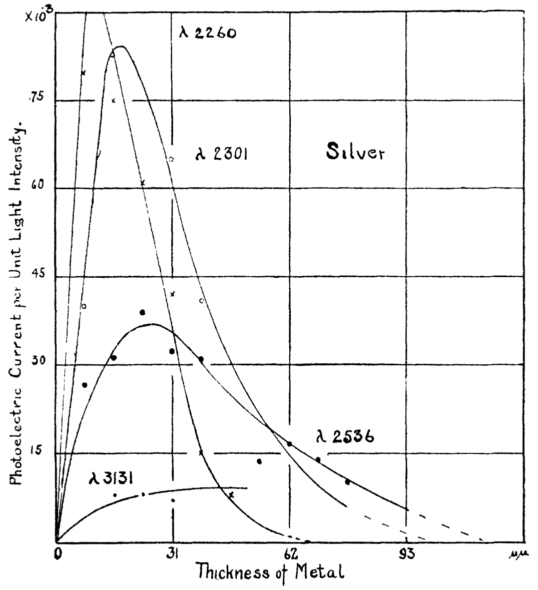

Fig. 5.

Figs. 4 and 5 show a typical set of observations for each of the metals. To avoid the error that might be introduced by photoelectric fatigue it was found necessary to prepare a separate wedge of metal for the observations obtained for each wave-length examined.

The photoelectric observations could be duplicated with a mean error of five per cent., but since the thickness determinations possessed an average error of ten per cent., no additional precautions were introduced into the photoelectric measurements to insure a greater accuracy. The constants computed from these curves show a degree of consistency in agreement with the above errors, which serve as a good check on the observational values.

In Fig. 4 the dotted line for λ 2536 gives the unfatigued values of the photoelectric current computed from the solid fatigued curve just below it. The ordinates of this curve were obtained by increasing the observed fatigued values by an amount experimentally determinable and proportional to the time elapsing between the removal of the wedge from its vacuum chamber and its subsequent photoelectric examination.

The curves for both metals have this in common; all make finite angles with the abscissa. There is no sign of inflexion on the ascent of the curve, so that the tangent to the curve at the origin is more inclined to the abscissa than the tangent at any other point. This means that for the very thinnest part of the wedge (atomic thickness) the photoelectric effect occurring there for any frequency of the exciting light, bears a definite ratio to the mass per square centimeter of the film. The slopes of the curves at the origin are relative measures of the energy absorbed by a film thickness comparable to the diameter of one molecule.

The curves can, for the sake of discussion, be divided into two parts. The initial rise which appears to be a type of saturation curve, and superimposed upon this a second phenomena of a more complex nature approximately represented by an exponential drop followed by a linear relation ending in another less rapid fall.

These two phenomena will be treated separately under the subject of scattering and absorption of photoelectrons.

The photoelectric current is excited by a monochromatic beam of light falling normally on the metal surface, and if no electronic absorption takes place the photoelectric current should be proportional to the light energy absorbed. If the optical constants of the metal do not change with change in film thickness for the wave-lengths used, it would follow that as the thickness of the metal increases linearly the photoelectric current should increase exponentially. This would continue until a thickness is attained beyond which the monochromatic light could no longer penetrate. This does not however hold true. When we measure the emergence effect, the curves seem to indicate that the light gives rise to electrons in amount apparently greater than the amount of light absorbed. It becomes therefore necessary to determine the cause of this additional electronic activity.

THEORY.

For the sake of simplicity let us consider only those electrons which leave the atom in the emergence direction, possessing energy proportional to the frequence of the exciting light but independent of the kind of atom from which they initially escape.

As the liberated electrons pass through successive layers of matter, let us further assume for simplicity that they are absorbed according to an exponential law.

If then a beam of light of frequency ν strikes a metal film, and if I_0 is the intensity penetrating the surface normally, if the intensity has fallen to I after passing through a thickness dx, then

$$I = I_0 e^{-\epsilon x}.$$

If all of the absorbed energy is used in liberating photoelectrons in such a way that the energy absorbed is equal to the photoelectric energy liberated then

$$I_0 - I = I_0(1 - e^{-\epsilon x}), \tag{3}$$

where ϵ is a constant, denoting the rate of appearance of electrons. It depends on the frequency of the light used and may be identified with the coefficient of absorption of the light. Since electronic density and light intensity are proportional under these circumstances, I_0 can be considered a variable, subsequently to be absorbed exponentially in the distance $t - x$. Then

$$\frac{dI_0}{dx} = -\alpha I_0$$

where α is the coefficient of absorption of the electrons passing through thickness $t - x$. The solution of this relation is given by

$$I_o = I' e^{-\alpha(t-x)}.$$

Since all the electrons due to any frequency ν of the light have the same initial velocity and hence may initially be considered a homogeneous beam coming from a layer of metal between x and $x + dx$, it follows if we assume that only those electrons are considered that move off in the emergence direction, that the intensity of the emergence radiation is proportional to

$$\frac{dN}{dx} = \epsilon I_0 e^{-\epsilon x} = \epsilon I' \int_0^t e^{-\epsilon x} e^{-\alpha(t-x)} dx$$

and

$$N = \frac{\epsilon I'}{\alpha - \epsilon}(e^{-\epsilon t} - e^{-\alpha t}). \tag{4}$$

It is seen that for small thicknesses the photoelectric current is proportional to the thickness or number of atoms per cubic centimeter. With increased thickness the curve passes through a maximum when

$$t_m = \frac{1}{\alpha - \epsilon} \log_e \frac{\alpha}{\epsilon} \tag{5}$$

and apparently decreases exponentially with the intensity $I' e^{-\epsilon t}$.

In order to determine to what extent the above curves check this theory the discussion is for convenience divided into two parts, the initial absorption of light as a function of the thickness and the absorption of the photoelectrons as determined by that part of the curve showing the decrease of the photoelectric effect with its subsequent disappearance as the thickness increases.

ABSORPTION OF LIGHT WITH VARIATION IN THICKNESS.

If under the experimental conditions outlined above, the photoelectric current is represented for any thickness t, by the relation $I_0(1 - e^{-\epsilon t})$ then this is equivalent to saying that the intensity of the electronic radiation from a unit area of the metal is always proportional to the number of atoms present in one cubic centimeter. The values of ϵ therefore obtained from these curves would help to determine the validity of this relation. If the number of electrons liberated are proportional to the amount of light absorbed, and if the metal film is so thin that the absorption of the electrons as they pass through the successive layers of molecules can be neglected, then successive similar layers of the metal will absorb equal fractions of the amount of light energy they receive, provided no scattering takes place, and emit a quantity of electronic energy which is a measure of the light energy absorbed. Under these conditions we can measure the electronic energy and use it as a measure of the light energy absorbed. If then we let ϵ represent this coefficient as measured

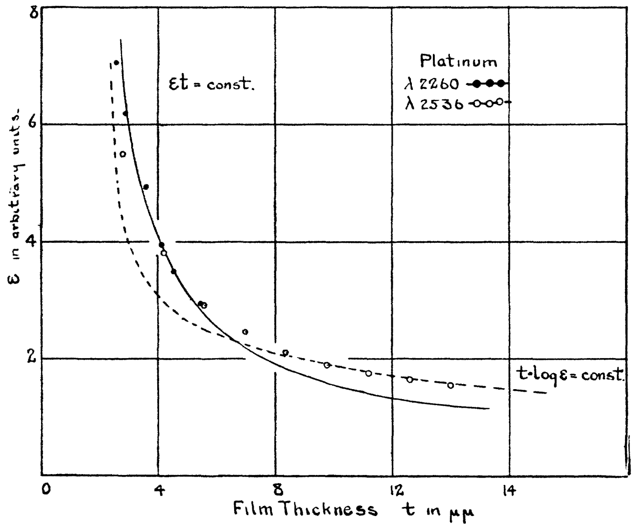

Fig. 6.

by the electronic results, I_0 the intensity of the energy entering the slab of material, I the intensity leaving, then $I = I_0 e^{-\epsilon t}$ where t is the thickness of the slab. This may be rewritten in the form

$$\epsilon = \frac{2.3}{t} \log \frac{I_0}{I}$$

If now $\log I_0/I$ is plotted against t, the graph should be a straight line (for ϵ constant) and ϵ may be determined from the relation $\epsilon = 2.3 \times$ slope.

The curves thus obtained were however not linear, they showed a continuous decrease in the coefficient ϵ (Fig. 6) as the thickness increased. The coefficients were then computed from the photoelectric curves using the relation $\epsilon = 0.693/D$ where $e^{-0.693} = 0.5$ and D is the thickness which reduces the radiation to half value. Here $1/\epsilon$ represents the distance to which the energy penetrates before its intensity is reduced $1/e$ of its original value.

TABLE I.

Platinum, λ2301.			Silver, λ2301.		
t.	ϵ.	ϵt.	t.	ϵ.	ϵt.
1.40 $\mu\mu$	.990 $\mu\mu^{-1}$	1.39	1.70 $\mu\mu$	.393 $\mu\mu^{-1}$	.668
2.10	.660	1.39	2.54	.260	.660
2.70	.520	1.40	3.30	.206	.679
3.50	.396	1.38	4.25	.160	.680
4.20	.330	1.39	5.00	.135	.665
5.05	.283	1.43	5.77	.114	.657
5.90	.230	1.35	6.90	.100	.690

TABLE II.

Platinum, λ 2536.

t.	ϵ.	ϵt.	$t \log \epsilon$.
2.8 $\mu\mu$	.550 $\mu\mu^{-1}$	.154	264
4.2	.381	.160	244
5.6	.291	.163	260
7.0	.247	.173	275
8.4	.211	.177	273
9.8	.190	.186	273
11.2	.176	.197	276
12.6	.165	.208	273
14.0	.157	.216	271

The above extended values give some idea of the general trend of the results. From the samples cited in Table I. it is seen how very close the product ϵt approaches a constant for small values of thickness. The constancy of this product was found to hold, in the case of both platinum and silver for λ 2260 and 2301, so long as the values thus obtained remained associated with very small values of *t*. When the thickness became larger ϵt no longer remained constant but increased with increasing values of *t*. A characteristic set of observations illustrating this condition is cited in Table II. If however, the relation $t \log \epsilon$ is computed from the data it is found that this relation is constant for large values but not for small values of *t*. As an example the case of Pt λ 2536 is cited, the change taking place at thickness 7 $\mu\mu$.

One characteristic common to all these results is that ϵt seems constant under two circumstances, either for quite a range in values of *t* for large values of electronic velocities, excited by means of λ 2260 or 2301, or for a very short range in the values of *t* (about 7 $\mu\mu$) when slower electronic velocities are used, as for example those excited by λ 2536 or 3131. Although the curve for platinum λ 3131 is shown in Fig. 4, yet the coefficients calculated from this curve were omitted owing to insufficient points on the curve to determine its initial slope. In addition the minimum wave-length sensibility for platinum is just inside the wave-length used so that the above curve must have been obtained through part of the shorter wave-lengths in the spectrum overlapping this region. The value for silver λ 3131 has only been introduced to show the order of magnitude of the value ϵt.

TABLE III.

Mean Values of ϵt *= const. for small values of* t.

λ.	*Pt.*	*Ag.*	**Ratio.**
2260	1.41	.681	2.07
2301	1.39	.671	2.07
2536	1.61	.983	1.64
3131		1.80	
Atomic weights	195.2	107.9	1.82

A summary of these results for values of *t* small, representing mean values similar to the extended data given above are shown in Table III. The last column gives the ratio of the values for this relation. It is of the same order of magnitude as the ratio of the atomic weights. We might conclude that the light energy absorbed per atom, is proportional to its atomic weight.

Before going into the possible origin of the above relations it may be of interest to examine the constancy of the relation ϵt further. The values of *t* were therefore plotted against values of $1/\epsilon$ (Fig. 7). Under these conditions one would expect to get a straight line whose slope would give a relative measure of the absorption of the light in passing through a molecular layer.

Since the amount of light energy absorbed is proportional to the photoelectric energy liberated it follows that the values of ϵ determined for changes in thickness, are also measurements of the photoelectric characteristics. Under these conditions we may view the electron as liberated from its parent atom, passing through successive layers of molecules being deflected through collision with them but never entering the system of the atom to disappear through absorption.

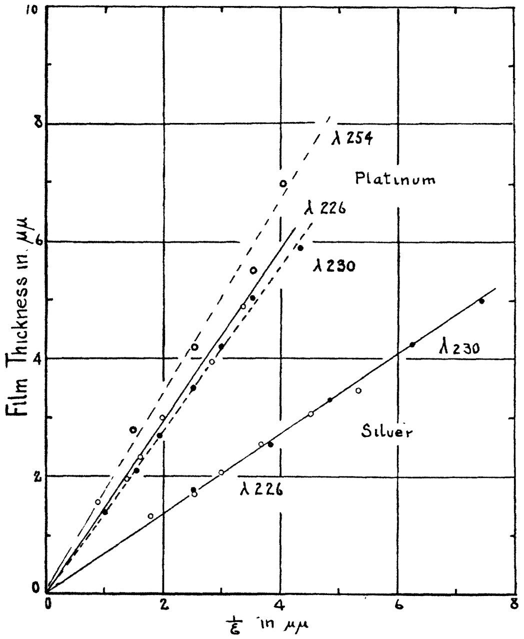

Fig. 7.

If therefore we consider two electrons, liberated with the same initial velocity, in the two metals, we will find after having passed through equal thicknesses of metal that the electron must have undergone a greater energy change per unit distance in passing through platinum than through silver. This ratio is, within experimental error, the same as the ratio of the densities of the two metals. This means that if equal masses are compared the amount of energy scattered is the same in the two cases. A similar relation exists for secondary radiation produced by Röntgen rays.[1] The above results are shown graphically in Fig. 7. In general they also seem to indicate that the greater the velocity of separation of

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[1] Barkla, Phil. Mag., 7, p. 543, 1904.

the electron from its parent atom, the less the scattering of its energy as it passes through neighboring atoms. The observations for platinum λ 226 do not fall in line with this conclusion. This exception can however be attributed to experimental error. The results for Ag λ 254 are here omitted so as to prevent too much crowding in the figure. The results for λ 226 and 230 lie so close together that it is impossible to separate them in the graph, though the actual results from which the curve is compiled show that λ 230 lies to the left of the results for the smaller wave-length.

If ϵ represents the fraction of the total light energy lost through absorption and reappearing as electronic energy, in going through a sheet of metal of molecular thickness t, I_0 the intensity of the beam entering the sheet and I the intensity of the beam leaving it, then $1/\epsilon$ the intensity coming out of the sheet is given by

$$\frac{I_0 - I}{I_0} = \frac{1}{\epsilon} = kt, \tag{6}$$

where k is a constant. From which we get

$$I = I_0(1 - kt). \tag{7}$$

For larger values of t under the same circumstances it was found experimentally that

$$t \log \epsilon = \text{const.},$$

then

$$\frac{I_0 - I}{I_0} = \frac{1}{\epsilon} = e^{-c/t}, \tag{8}$$

or

$$I = I_0(1 - e^{-c/t}). \tag{9}$$

These relations do not however conform to our simple theory advanced at the beginning of the paper which involved the assumption of an exponential absorption leading to equation (4).

THEORY OF SINGLE AND COMPOUND SCATTERING.

Rutherford[1] has advanced a theory of single scattering which leads to the conclusion that the proportion I/I_0 of the rays which remain undeflected after passing through a thickness t, when t is small enough,[2] is given by the relation

$$I = I_0(1 - kt).$$

A relation deduced from the above experimental data for thicknesses less than 7 $\mu\mu$ (Fig. 6).

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[1] Rutherford, Phil. Mag., V., 21, p. 684, 1911.

[2] Richardson, Electron Theory, p. 496.

For very small thicknesses we must therefore have electrons passing through the metal film, colliding according to Rutherford's hypothesis of "single scattering" and little or no energy is contributed to the atom through which the electrons passed. From this it is seen that the relation between I/I_0 and t should be nearly linear in the initial stage, and this is found to be the case for all wave-lengths for both metals investigated.

If however the thickness penetrated by the electrons becomes greater a larger number of collisions necessarily results, and then the relation $t \log \epsilon = \text{const}$ expresses the state of affairs. It seems as if the electron might be considered as at first moving in fairly straight lines with little deflection and little or no energy exchange, but as the penetration increases the deflexions become more numerous and violent resulting in the rate of expenditure of energy increasing so rapidly that the electron seems to come to a sudden stop.

This stage of the process seems to be equivalent to what Thomson[1] describes as "compound scattering." He showed that the probability of an average deflexion of an electron on passing through a metal sheet of thickness t, if less than a given angle, is equal to $1 - e^{-c/t}$ where c is a constant for any particular substance, which under the present experimental circumstances means that the proportion I/I_0 of the electrons undeflected is given by $I = I_0(1 - e^{-c/t})$ a relation identical with the empirical equation (9).

The experimental arrangement and method therefore appears to fulfill the requirements for single scattering when the metal films are very thin (less than 7 $\mu\mu$), and compound scattering when the metallic film is thicker (Fig. 6).

In these experiments the angular opening ϕ through which the electrons escape from the film is not varied, and if the same metal be examined so that the absorbing medium is also kept the same and the velocity of the electrons varied through change in wave-length of the illumination both Rutherford's and Thomson's theory leads to the relation,

$$\frac{mv^2}{t_0^{1/2}} = \text{const.}, \tag{10}$$

where t_0 is the value of the thickness required to cut down the radiation to half value.

This relation can be tested with film thicknesses in which single scattering takes place. In the experimental arrangement ϕ is kept constant. Now the maximum energy of release of the electron is independent of the kind of atom and only depends on the frequency of the exciting light.

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[1] Camb. Phil. Proc., 15, p. 465, 1910. See Richardson, Electron Theory, p. 493.

If therefore we consider values of $1/\epsilon$ for equal values of t_0 and λ in the two metals, we have a measure of the relative average energies with which the electrons appear after passing through equal thicknesses. This also gives us a comparison of the distances to which electrons penetrate so as to have their initial energies reduced to $1/e$ of their original value. The results obtained from the data as shown in Fig. 7 indicate that equation (10) is valid within experimental error for film thickness less than 10^{-7} cm.

An interesting and rather important change takes place after the electron penetrates further into the metal. In Fig. 6, we see an illustration of the thickness at which this occurs. We are here confronted with another illustration of the sudden change in the property of a metal when its thickness is less than 10^{-7} cm. Similar changes occur in the optical and electrical properties of these metal films in this immediate vicinity.[1]

Unfortunately not enough data were available from individual results for λ 2536, to show clearly that the smaller values of t followed the ϵt = const. relation (Fig. 6), so that the values for λ 2260 were added to show how close the results fitted the theoretical curves, here shown as solid and broken lines. The latter results were therefore shifted so that the axes of the curve coincided with the axes of the curve for values λ 2536. In this way the results show graphically just where the region of separation exists to which the above theories apply.

If we now consider thicknesses in which compound shattering exists we are limited on one side by the thickness comparable to 7×10^{-7} cm. and the maxima of the curves shown in Figs. 4 and 5. As seen from the sample data shown in Table II. the coefficient decreases less rapidly than the increase in thickness. This is to be expected, if the above theory can be applied; for the amount of scattering becomes more marked with decrease in speed and increase in thickness. This continues until a critical thickness is reached where the absorption of the number of electrons becomes predominant, finally leading to a decrease in the amount of emergence radiation.

The initial rise in the curves can therefore be divided into two distinct regions. For thicknesses less than 10^{-7} cm. the velocities of the emergence electrons must be nearly equal or so nearly that very few if any electrons appear whose energy is less than that demanded by the Einstein relation. Here little if any absorption takes place so that the electron passes through subsequent layers with slight loss of energy. From here on however the number of electrons possessing less than this maximum energy decreases, they undergo frequent and violent collision

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[1] Patterson, Phil. Mag., IV., p. 663, 1902. Minor, Ann. d. Phys., 10, p. 581, 1903.

with a rapid loss in energy until some electrons seem to come to a sudden stop. Further penetration is then accompanied by loss in numbers in addition to loss in energy.

Absorption of Photoelectrons.

Our theory as outlined at the beginning of the paper indicated a maximum for values of t given by the relation

$$t_m = \frac{1}{\alpha - \epsilon} \log_e \frac{\alpha}{\epsilon}.$$

The values for t_m as picked off of the ionization curves are given in Table IV., Fig. 8. The values of t_m there indicated represent the distances to

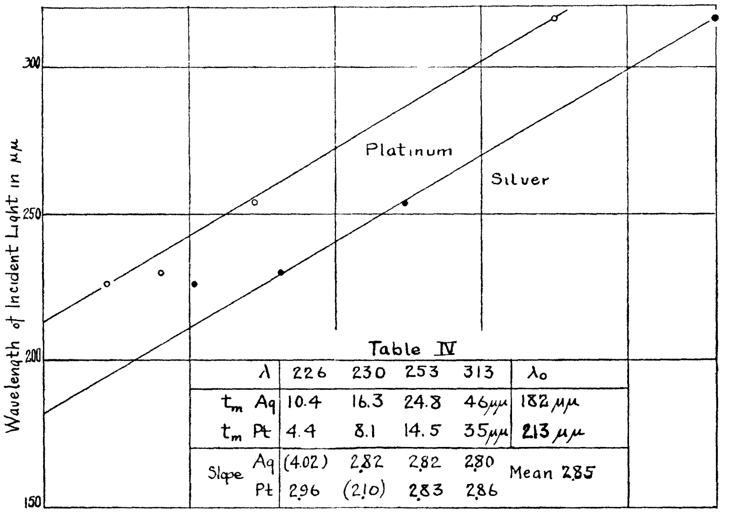

Table IV

	λ	226	230	253	313	λ_0
t_m	Ag	10.4	16.3	24.8	46$\mu\mu$	182 $\mu\mu$
t_m	Pt	4.4	8.1	14.5	35$\mu\mu$	213 $\mu\mu$
Slope	Ag	(4.02)	2.82	2.82	2.80	Mean 2.85
	Pt	2.96	(2.10)	2.83	2.86	

Fig. 8.

which an electron, starting from the lowest layer with initial energy $\frac{1}{2}mv^2 = h\nu$, can penetrate, before it disappears through absorption. The distance t_m is here called the scattering range. It does not measure the actual distance pursued by an electron in the form of the summation of all the zigzag paths, but the distance perpendicular to the surface of the metal. The values obtained in this way are plotted as a function of the wave-length of light causing the separation of the electron from its parent atom. The slope of the curve is the same for the two metals, the bracketed values in the table are however marked exceptions to this rule. The cause for this unusual difference cannot be accounted for through experimental error. It seems likely however that the straight line relation is perhaps a first approximation to the truth and more numerous data determined for longer and shorter wave-lengths than here investigated will determine to a more exact degree the necessary relations.

The present curves however fit the relation $\lambda - \lambda_0 = at_m$ to a marked degree. Here a is the slope of the curve and equal to 2.85, λ_0 is the value of the minimum wave-length producing electrons possessing an effective scattering range equal to zero. This would mean that λ_0 would be the minimum wave-length limit which could produce a photoelectric current under the above experimental conditions. Higher frequences might liberate electrons, but their energies would be so great that they could penetrate the next atoms in their path and completely disappear in their system. These electrons would be absorbed so promptly that we could expect a metal to possess the property of selective absorption for electrons possessing these critical velocities. The minimum wave-lengths of the incident light energy producing electrons under these conditions are 213 and 182 $\mu\mu$ for platinum and silver respectively.

TABLE V.

	Velocity $\times 10^{-7}$ Cm. per Sec.				Mean Velocity.	λ_0.
λ in $\mu\mu$.	226.	230.	253.	313.		
Silver	14.5	14.0	13.3	13.5	13.8×10^7	182 $\mu\mu$
Platinum	14.1	13.8	13.2	13.4(?)	13.6×10^7	213 $\mu\mu$
$v = \sqrt{\frac{2h\nu}{m}}$	14.05	13.95	13.25	11.92	$\times 10^7$ cm/sec	

If however the above wave-length relation is reduced to its equivalent energy form we have

$$\frac{1}{v^2} - \frac{1}{v_0^2} = bt_m, \tag{11}$$

where $b = 1.42m/hc$, assuming the relation $\frac{1}{2}mv^2 = h\nu$ to hold in the above case. We define m as the mass of the electron h as Planck's element of action and c as the velocity of light. Under these conditions v would be the velocity the electron must possess, to be able to penetrate a thickness t_m. Table V. shows the initial velocities the electrons should have, to penetrate thickness t_m, as computed from equation (11) and the velocities computed from the Einstein photoelectric equation. The contact difference of potential is here assumed equal to zero, since t_m is defined as the distance the electron travels in the metal without passing through the contact difference of potential layer. This use of the value of t_m is however not rigidly true but owing to lack of further information it is offered as an approximate solution. We see in Table V. to what extent the values for the computed velocities check the experimental values. In all cases the velocity decreasing with increased wave-length of the exciting energy.

Now $1/t_m$ may be defined as the stopping power. So that the stopping power of the metal increases as the energy of the electron increases, to eventually approach a limiting value. Comparing these values we note that the heavier the atom the greater the stopping power. If we therefore compare the distance traveled in platinum to that in silver for electrons of equal initial velocity we find that the distance traveled in silver is 1.17 as great as that in platinum when the energy in each is reduced to the same amount. Hence if we compare equal volumes of the material traversed we find that the ratio of the atomic volumes of silver to platinum is 1.13 or of the same magnitude as the relative distances traveled in the two metals. So that electrons after traversing equal masses have their initial energies reduced to the same extent.

Absorption Coefficients.

After passing through a thickness t_m the photoelectric thickness curve falls off slowly at first, then nearly linear and finally more slowly again cutting the thickness axis at what appears to be a finite value. Unfortunately the latter part of the curve was very difficult to determine

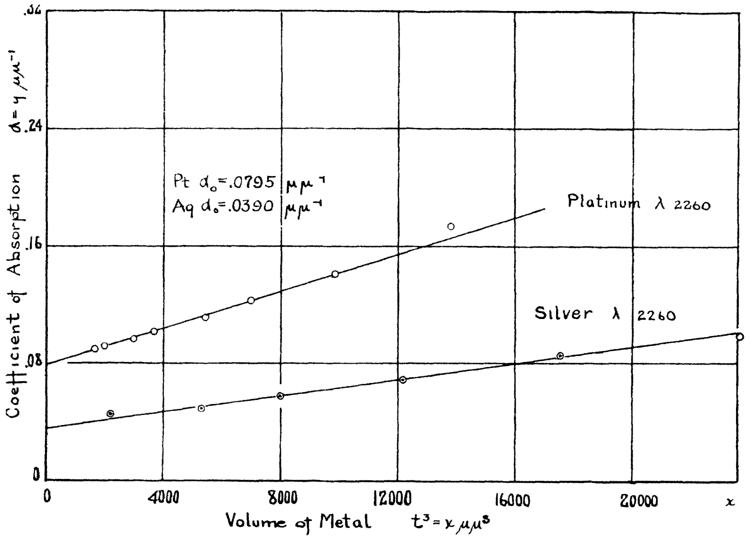

Fig. 9.

owing to the very minute number of electrons coming through such thick metallic layers.

The initial drop of the curve seems to indicate that there is little absorption of electron numbers as yet and that scattering is still predominant. From here on however the curve takes a very definite form. The problem is a very complex one, the steam of photoelectrons which are traveling in any given direction must suffer loss in numbers both through true absorption and scattering to such a degree as to completely disappear from the original direction and in doing so must lose energy as well. What the relative importance of these actions is in the present case is difficult to tell. A partial solution is however attempted.

The coefficients of absorption α were computed in the usual way for the absorption branch of the curve. These results were then plotted as ordinates and values of t, as abscissæ. The curve approximated nearest to a straight line when values of t^3 were used as shown in Fig. 9. Thus the relation $\alpha - \alpha_0 = mt^3$ would represent the relations to a comparative degree of accuracy limited by the experimental errors in the original observations. The values computed for α and values for m, the slope of the curves, are given for comparison, to show to what degree of accuracy the results may be valid.

TABLE VI.

Platinum, λ 226.			Silver, λ 226.		
a.	*t.*	*m.*	*a.*	*t.*	*m.*
.167 $\mu\mu^{-1}$cm^{-1}	24.0 $\mu\mu$	63.0 $\mu\mu^{-3}$cm^{-3}	.099 $\mu\mu^{-1}$cm^{-1}	29.5 $\mu\mu$	23.4 $\mu\mu^{-3}$cm^{-3}
.141	21.5	62.8	.083	26.0	25.0
.123	19.2	62.3	.070	23.0	25.4
.112	17.5	61.6	.059	20.0	25.0
.102	15.5	61.9	.050	17.5	20.5
.0972	14.5	60.0	.043	12.8	20.0
.0917	12.6	61.2			
.0907	11.8	68.0			
	Mean	62.6 $\mu\mu^{-3}$cm^{-3}		Mean	23.2 $\mu\mu^{-3}$cm^{-3}

The coefficients of absorption thus obtained are not constant, but increase very rapidly with increasing values of thickness traversed. The intercepts on the y axis are however of interest. They would represent the absorption coefficients for values of thickness commensurable to a molecular layer. These values of α_0 for platinum and silver were found to be .0795 and .0390 $\mu\mu^{-1}$ respectively for photoelectrons emitted with a velocity of 13×10^7 cm. per sec. from their parent atoms. If we divide the above values by the density of the respective metals to which they apply we arrive at the following interesting relation

$$\left(\frac{\alpha_0}{\rho}\right)_{\text{Pt}} = 37{,}000 \text{ cm}^2\text{gm}^{-1},$$

$$\left(\frac{\alpha_0}{\rho}\right)_{\text{Ag}} = 37{,}100 \text{ cm}^2\text{gm}^{-1},$$

showing the mass absorption to be constant for λ 226. This is the "density law" of absorption at first suggested by Lenard.[1] Crowther,[2] experimenting with β rays from uranium showed that the "density law" did not hold for these larger velocities. Lenard experimenting with heterogeneous cathode rays arrived at the following values for the metals gold and silver here given for comparison.

$$\frac{\alpha_0}{\rho} = 2880 \text{ cm}^2\text{gm}^{-1},$$

$$\frac{\alpha_0}{\rho} = 3070 \text{ cm}^2\text{gm}^{-1}.$$

Compton and Ross working with sputtered platinum obtained from photoelectric measurements the average value $\alpha/\rho = 28{,}900$. While Partzsch and Hallwachs (*l. c.*), using some data supplied by Rubens and Ladenburg, obtained the value $\alpha/\rho = 47{,}400$ for gold in the form of a leaf of about 100 $\mu\mu$ thickness.

The exigencies of the times have interrupted the completion of this subject at this time, it is hoped however that in the near future further data can be published which will support the above conclusions. The experimental part of this paper was performed at the University of Pennsylvania and I take great pleasure in acknowledging the ever generous coöperation of Prof. Goodspeed in furnishing the funds for the necessary apparatus.

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[1] Lenard, *l. c.*

[2] Crowther, Phil. Mag., 12, p. 379, 1906.

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