ON THE ASYMMETRIC EMISSION OF PHOTO-ELECTRONS FROM THIN FILMS OF PLATINUM. I.

BY OTTO STUHLMANN, JR.

INTRODUCTION.

AS early as 1889, W. Hallwachs[1] showed that a photo-electric effect could be obtained from a silvered quartz plate when light was incident through the quartz.

Later Rubens and E. Ladenburg[2] took up the work and observed a similar effect for gold leaf. They found the ratio of the photo-electric effect for incident and emergent light to be 100 to unity while the fraction of the ultra-violet light transmitted, photo-electrically measured, was one one-thousandth of the incident.

The work was taken up by the writer[3] who showed that the photo-electric effect of thin cathode films of different metals deposited on quartz depends on the thickness of the film and whether the film is on the side of the quartz facing the light (incident effect = I) or on the side away from the light (emergent effect = E). The ionization currents were measured in air. It was shown that when the films are thin enough, about 10^{-7} cm. or less, that the ratio emergent to incident currents (E/I) was greater than unity and for thicker films less than unity. This ratio was constant for thin films and was shown to be equal to 1.17 for platinum.

Independent experiments carried out by R. D. Kleeman[4] both in hydrogen and in vacuo led to the same conclusion as to the asymmetry of the photo-electric effect for emergent and incident light.

Recently J. Robinson[5] showed that the above observed dissymmetry of emission should be separated into two quite distinct effects; the actual number of electrons emitted and the velocities of the electrons emitted.

AS TO THE ACTUAL NUMBER OF THE ELECTRONS EMITTED.

It was shown by Robinson[6] that the magnitude of the ratio of emergent to incident current depended upon the source of illumination. When the

[1] W. Hallwachs, Tagebl. d. Heidelberger Nat.-Vers., S. 24, 1889.
[2] Rubens and E. Ladenburg, Ber. d. D. Ges., 24, p. 749, 1907.
[3] O. Stuhlmann, Jr., Phil. Mag., 20, p. 854, 1911.
[4] R. D. Kleeman, Proc. Roy. Soc., 84, p. 92, 1910.
[5] J. Robinson, Phil. Mag., 23, p. 542, 1912. Pt. II., Phil. Mag., 25, p. 115, 1913.
[6] Loc. cit., Pt. II., p. 125.

films were illuminated by a spark between brass terminals the ratio of emergent to incident effect was equal to 1.27, while a mercury vapor arc in quartz changed the value to 1.16. An iron arc as originally used by the writer gave 1.17 for this ratio. More recent results show a change in this value in a decreasing order of magnitude as follows: iron arc, quartz mercury vapor lamp, iron spark, zinc spark and cadmium spark in air.

The current curves plotted against film thickness show a maximum at about 10^{-7} cm. For thin films the emergent being greater than the incident effect. The rate of increase, however, does not take place so suddenly as Robinson's curves lead one to think. A more careful study of the change of current with film thickness as shown by the writer and K. T. Compton,[1] attributes the sudden tremendous increase in current, to method of making contact between film and holder when the plates are sputtered in vacuo.

Recently Partzsh and W. Hallwachs[2] became interested in this question from an optical point of view. They investigated a series of cathode deposited platinum films ranging in thickness from 1 to 50$\mu\mu$. The incident, reflected and transmitted beams were measured both for emergent and incident positions. If the film were illuminated so that the transition layer was quartz-platinum, 40 per cent. more light was absorbed by the film than when the illumination fell directly on the metal side. They further showed that the reflection coefficient for the transition layer quartz-platinum, at first decreased with increasing thickness of film to about 3$\mu\mu$ where a minimum occurred. Then increased until at 7$\mu\mu$ the original value recurred. A further increase in thickness was accompanied by an increase in the reflection coefficient until it approached the value for platinum. From these data in connection with the values of the variations in transmission with change in thickness of film one may plot the absorption curve.

Since absorption of light and photo-electric current are proportional, one would expect these curves to be identical with the ones obtained by measuring the photo-electric current with change in thickness.[3] This, however, is not quite true, because the photo-electric effect shows a peculiar sudden[4] increase in current and then a well-defined minimum, which the curves by Partzsh and Hallwachs do not account for.

They further show that thin platinum films on quartz, whose thickness is less than 10^{-6} cm., absorb, when illuminated through the quartz plate,

[1] O. Stuhlmann, Jr., and K. T. Compton, PHYS. REV., S. 2, Vol. II., p. 205, 1913. Pt. II., PHYS. REV., S. 2, Vol. II., p. 327, 1913.

[2] Partzsch and W. Hallwachs, Ann. d. Phys., 41, p. 247, 1913.

[3] Stuhlmann and Compton, PHYS. REV., S. 2, Vol. II., p. 208, 1913.

[4] For a possible explanation of this see J. Robinson, Phil. Mag., 25, p. 127, 1913.

1.5 to 1.4 times as much of the incident light as when the illumination falls directly on the platinum. These differences, the authors conclude, are great enough to account for the ratio of the emergent to the incident effect as photo-electrically measured by Kleeman, Robinson and the writer.

It was thought by some writers, since the ratio of the emergent to the incident effect was greater than unity, that the emitted electrons received a velocity component in the direction of the propagation of the light. A longitudinal action of the light, if present, is evidently of a smaller order of magnitude than the above photo-electric ratios, of emergent to incident currents, seem to indicate.

As to the Velocities of the Electrons Emitted.

The maximum velocities of emission, for platinum cathode films deposited on quartz, were also investigated by J. Robinson.[1] He found that for very thin films (less than 10^{-7} cm.) the maximum velocity of emission due to the emergent light was greater than that due to the incident light; for thicker films the reverse was found to be true. In his first paper the maximum value for the ratio of emergent to incident velocities, as obtained by projecting his curve backwards, gives 1.24, while his second paper shows only 1.12 for this maximum value, although the same apparatus and source of illumination were used.

Since the maximum energies of emission are independent of the intensity of the source of illumination, Partzsh and Hallwachs[2] conclude that the variation in absorption of the two positions of the films would be no adequate explanation of this observed change in velocity.

Robinson also determined the distribution of velocity curves for four samples of platinum films of different thickness. Partzsch and Hallwachs believe that objections might be raised to these results, in so far as values for the velocities were obtained only at two volt intervals, hence making any conclusions that might be drawn from the curves doubtful.

Concerning the Velocities with which Photo-electrons are Emitted from Matter.

An interesting and valuable suggestion was recently made by Mr. A. Ll. Hughes[3] concerning the velocities with which photo-electrons are emitted from matter. In his review of the literature on the subject of emission of photo-electrons from metallic surfaces, he emphasizes the

[1] Loc. cit.

[2] Loc. cit., p. 267.

[3] A. Ll. Hughes, Phil. Mag., 25, p. 683 (1913).

fact that the maximum velocities investigated were always those of electrons emitted from the side of the plate on which the light was incident. Under these conditions the Plank constant (h) as experimentally determined by the application of the Einstein-Richardson[1] equation, for the photo-electric effect, was always found to be less than 6.55×10^{-27} ergs sec., by an amount ranging from 10 to 25 per cent. Robinson[2] in his experiments on very thin platinum films shows that the velocities of the electrons for emergent light are greater than those for incident light, for thicker films the reverse is the case. For a certain thickness of film the emergent velocity is equal to the incident velocity and special experiments showed that for the same thickness of film the emergent current is equal to the incident current. The orientation of the plane of polarization of the light did not have any influence on the dissymmetry.

It may be inferred that originally all the electrons are, perhaps, emitted more or less in the direction in which the light is traveling and that the energy lost by a photo-electron in swinging round from its original direction of emission is at least comparable to the per cent. increase of the emergent over the incident effect. For an infinitely thin film this difference as shown by Robinson is about 12 per cent. Introducing the correction suggested by the asymmetric emission, Hughes concludes that the experimental and theoretical results may be made to check in the case of platinum, and presumably in other cases also, if we keep in mind the electrons which emerge in the direction of the incident light.

H. S. Allen[3] suggests that if this be borne out by further experiments, we reach the important conclusion that for light of a given frequency, electrons acquire the same energy in the case of all metals, though the work done in escaping is a quantity characteristic of the metal.

No experimental results as to the ratios of the emergent to the incident velocities for other metals are available and so it is not possible, at present, to test this view further. More precise information would be obtained if the ratios were investigated using monochromatic light. In view of these suggestions a further study of the velocities of emission from thin metal films was warranted.

PART I.

The first part of this paper is devoted to a solution of some of these questions. With this object in view Robinson's design of apparatus was practically adopted, in order, first to determine if his results could be

[1] O. W. Richardson, PHYS. REV., Vol. 34, p. 146 (1912); Phil. Mag., 23, p. 615 (1912); Science, 36, p. 57 (1912).

[2] Loc. cit.

[3] H. S. Allen, Photo-Electricity, Longmans, Green & Co., 1913.

duplicated, second to get the distribution of velocity curves for emergent and incident effect with change in thickness of the films.

APPARATUS.

The apparatus as shown in Fig. 1 consists of a heavy brass outer cylinder put to earth. Coaxial with it is a light brass cylindrical box (C) supported by a rod passing through a ground glass stopper B. A circular quartz plate Q, 1 mm. thick and 2 cm. in diameter, passing through the ground glass stopper R and insulated from it with hard sealing wax, projects into the inner cylinder. This quartz plate is covered with the platinum deposit in the form of a semi-transparent film and is attached to the rod by means of a screw clamp. The ground glass joint served to rotate the quartz plate through any angle so that the film may be made to face the light or be turned away from the light, in order to measure the photo-electric effect in these two positions. The inner cylindrical box (C) is 7.5×3.5 cm. over all, with circular openings at both ends, 2 cm. in diameter. The cylinder was connected to a potentiometer circuit P containing a Weston standard voltmeter reading to one one-thousandth of a volt. The electrometer, connected to the quartz plate carrying the platinum film, gave a deflection of 765 divisions per volt at a scale distance of one meter.

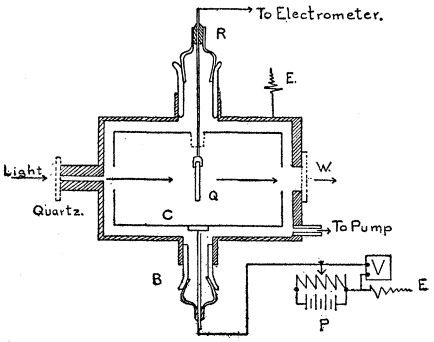

Fig. 1.

All the internal metal surfaces were covered with camphor soot to prevent effects due to stray reflected light.

A narrow beam of light from a quartz mercury vapor lamp stopped down to 3 mm., passed through a quartz lens (f 15 cm.) which focused the source on the platinum film. The beam entered the apparatus through a quartz window 1 mm. thick and passed out through a plate glass window at W. The quartz plate Q, carrying the metal film, the quartz window and the glass window at W, were all parallel and normal to the incident beam, so that any reflected light passed back along its entering path. This was obtained by rotating the plate Q until the reflected light passed through the forward opening.

The source of light was a quartz Cooper Hewitt mercury vapor lamp (Type Z) using 4 amperes direct current at 110 volts. It was found to be a reliable, very constant and brilliant source of illumination.

The platinum films were deposited from a circular platinum disk 5 cm. in diameter, in a separate glass chamber. From here they were introduced rapidly into the testing vessel. Previous experiences with these metal films having shown that such handling does not effect their photo-electric properties. Experiments by the writer and K. T. Compton[1] have shown that a cathode discharge, through the apparatus in which velocity measurements are to be made, may deposit films giving off electrons with spurious high velocities. Under these conditions the films may also show effects depending on the method of making contact between them and the holder, such results having previously been interpreted as properties of these cathode films. To insure against these effects the films were deposited in a separate chamber and mounted for examination in identical ways Through the control of the cathode fall and current Tyndall and H. G. Hughes[2] have conclusively shown that the thickness of the film is a linear function of the time.

A Gaede rotary mercury pump was used to furnish the desired vacuum. A gold leaf mercury vapor condenser was inserted just after the pump to prevent the mercury vapor from amalgamating with the platinum films. The results were all compiled from data taken at a pressure of 2×10^{-5} cm. or less.

VELOCITY MEASUREMENTS OF THE RATIOS E/I.

The maximum initial kinetic energy of the emitted electrons, expressed in equivalent volts was determined by charging the cylinder C to such a negative potential that the electrometer connected to the platinum coated plate Q, showed no deflection. The velocity v of an electron is connected with this maximum potential V by the relation $\frac{1}{2}mv^2 = eV$. The equivalent maximum potential taken up by the film was measured, when the film was turned to face the light (I) and when it was turned away from the light (E).

This maximum potential was corrected for contact difference of potential, since under the above conditions the electrons are driven back into the metal by a difference of potential equivalent to the contact difference of potential between the platinum and the surrounding metal case, plus the potential impressed by the outside circuit on the cylinder. The contact difference of potential was measured in air by means of the ionization method. For this purpose a tube containing 0.89 mg. of radium chloride was fastened against the window W and the potential measured to which the cylinder (C) had to be charged to produce no deflection. This method is very sensitive to changes in contact differ-

[1] Loc. cit.

[2] Tyndall and H. G. Hughes, Phil. Mag., 27, p. 415, 1914.

ence of potential and has been very successively used by K. T. Compton[1] and N. Shaw.[2]

It was found that very erratic results were obtained upon first introducing the films into the testing chamber. Separate experiments showed a gradual change to a steady state. This was shown to be due to the gradual drift of the contact difference of potential to its final value. For thin films this effect was more pronounced than for thicker films. The contact difference of potential rose rapidly to a maximum of several volts, from where, after several hours, it exponentially dropped to its final constant value. For very thick films or a metal plate no such maximum appeared, the curves rapidly rising to their normal value, giving identical results as those obtained by N. Shaw.[3] The following data were obtained after the steady state had been reached.

TABLE I.

Measurements of the Maximum Energy of the Electrons Produced by Incident and Emergent Light.

Relative Thickness of Film.	Emergent Light.		Incident Light.		Ratio of Emergent to Incident Energy Corrected for C.D.P.
	V. Max.	C.D.P.	V. Max.	C.D.P.	
1	.428	+.295	.212	+.298	1.42
2	1.000	.300	.565	.303	1.49
3	1.630	.254	1.667	.202	1.01
4	1.094	.322	1.224	.302	.927
5	.600	.356	.775	.337	.860
Pt. plate.	.....	.....	1.438	.353	.....

Table I. gives the ratios of emergent to incident kinetic energies corrected for contact difference of potential as obtained above. It was assumed that the measurements of contact difference in air would not differ appreciably from those measured in vacuo, under the same conditions. Characteristic results are only given, showing the variation in the ratio E/I with change in thickness. Numbers 1 and 2 are characteristic results from very thin transparent films whose thicknesses are less than 10^{-7} cm. Number 3 is quoted because of its unique value showing a film where the emergent and incident effects are practically the same. Numbers 4 and 5 show the change in the values of E and I to thick films, while the value for a freshly scraped platinum plate is given as a comparison standard.

It is evident that the films are of platinum since they possess practically the same contact difference of potential as the platinum plate.

[1] K. T. Compton, Phil. Mag., 23, p. 579, 1912.

[2] N. Shaw, Phil. Mag., 25, p. 241, 1913.

[3] N. Shaw, loc. cit.

They are consistent with previous results obtained along a different line[1] and agree with those cited by Robinson[2] except in so far as the ratios given above are a little larger. This is perhaps due to the fact that each of the above values is the mean of several determinations obtained by means of a null method of observation. They differ from Robinson's results in so far that these and previous results by the writer and K. T. Compton[3] show that a distinct maximum exists both for incident and emergent energies at a thickness comparable to 10^{-7} cm., where Robinson found his maximum for the current-thickness curves. After this maximum the emergent energy diminishes as the thickness of the film increases while the incident energy gradually increases to the normal value for platinum[4] as the thickness of the film increases. From the data of Partzsh and Hallwachs[5] one may plot the absorption curve for changes in thickness. No such pronounced maximum exists, as would account either for the sudden increase in current or velocity. The hypothesis of a longitudinal component in the light producing the asymmetry is highly improbable. The theory advanced by Robinson of a secondary effect coexisting with the liberation of an electron is one which has to be reckoned with. At any rate further information is desirable before advancing even a tentative hypothesis to explain the asymmetry in the velocity of emission.

VELOCITY DISTRIBUTION CURVES.

A curve giving the relation between the photo-electric current and the potential difference between the illuminated film and the surrounding case is called a velocity distribution curve.[6] When the potential difference is such as to retard the electrons then the photo-electric current is usually taken to be the measure of the number of electrons possessing velocities greater than that implied by the potential difference. If no contact difference of potential existed the ideal curve would saturate at zero potential.

It is well known that these velocity distribution curves are liable to distortion by reflection of electrons, but the value of the maximum velocity is not effected by them. If reflection of electrons by the surrounding case takes place the curve will be modified and depressed along

[1] O. Stuhlmann and K. T. Compton, PHYS. REV., S. 2, Vol. II., p. 205, 1913.

[2] J. Robinson, loc. cit.

[3] Loc. cit.

[4] Loc. cit.

[5] Loc. cit.

[6] For the theory of the "Velocity Distribution Curves" see A. Ll. Hughes, Phil. Trans. Roy. Soc., Lond., *A*, Vol. 212, pp. 205–226, 1912.

the current axis in proportion to this reflection, hence giving a slight negative current for potentials greater than the equivalent maximum velocity. Reflection of light also alters the shape of the curve, but this has been taken care of by blackening the interval surfaces with camphor soot. The photo-electric sensitiveness of this effect falls within the experimental errors. The effect of a stray magnetic field or of the approaching of the electrons to the surface in an oblique direction both tend to shift the curve.

With the existing apparatus experiments were made to determine how the velocity distribution curve normally obtained from solid metals under the above conditions was effected by the change in direction of the illumination on the metal film. Second to see if a change in thickness of the film was followed by a corresponding change in the slope of the curves analogous to the change in the absorption curves of Partzsch and Hallwachs. Third to determine whether the asymmetry of the maximum velocity could be substantiated by the relative magnitudes of the curves.

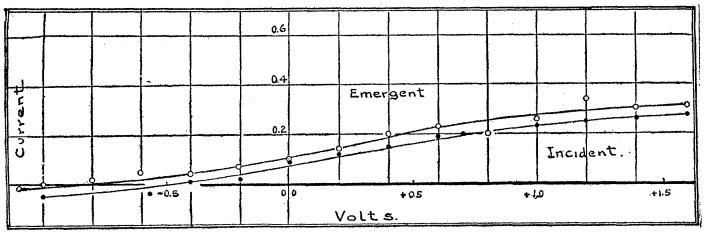

Fig. 2.

The films used were the same as those shown in Table I., for which the maximum velocities were determined. The observations were made at the same time as the previous values for the maximum velocity. The film was rotated to face the light when a definite potential difference was maintained between it and the cylinder and the speed of the electrometer index noted. The plate was then rotated through 180° so that the film was turned away from the light and the reading repeated. These readings for alternate emergent and incident effect were taken at 0.2 volt intervals. They could be checked by taking each curve separately.

The curves of Figs. 2 and 3 show this distribution of velocity among the electrons of films 1 and 2 in Table I., whose thicknesses are less than 10^{-7} cm. The ratio of the emergent to the incident effect throughout the whole range of potential is constant. This is significant in so far as it shows that the asymmetry for the maximum velocity can not be a spurious effect. This ratio can not be affected by any of the errors discussed above. If the emergent and incident curves are modified by the errors,

they will be equally affected, so that they will not influence the ratio E/I. The measurable currents are small so that the individual readings are susceptible to errors. Several readings were taken, for each point on the curves in order to reduce the average deviation to about 3 per cent. At any potential the number of electrons emitted for the emergent position are greater then the number from the incident position. This

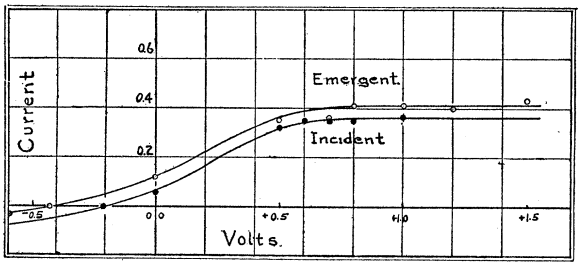

Fig. 3.

can be accounted for by the relative larger absorption of the film when facing away from the light than when turned towards the light.

The distribution of velocity curve for film 3 is given in Table II. The emergent and incident curves are too near alike to warrant a diagram to show the difference between the effects.

TABLE II.

Distribution of Velocity Curve for Film 3.

Difference of Potential in Volts.	Emergent Current. Divisions per Second.	Incident Current. Divisions per Second.
−2.0	−0.27	−0.16
−1.2	+2.5	+1.9
−1.0	4.8	4.0
− .8	6.4	6.3
− .6	15.0	12.0
− .4	19.4	20.0
− .32	25.0	19.0
− .2	30.0	25.4
∓ .0	38.0	33.7
+ .2	42.9	40.0
+ .32	45.4	44.1
+ .4	48.4	45.4
+ .6	50.0	48.0
+ .8	57.5	52.5
+1.0	65.9	57.5
+1.2	67.1	63.4
+1.6	71.8	69.5

$$\frac{E}{I} = \frac{1.884}{1.869} = 1.01$$

The number of electrons liberated are more than one hundred times as large as those from films 1 and 2. The saturation value of the current places this film just beyond the first maximum in the current-thickness curve.[1] Robinson showed that by plotting the ratio E/I for the maximum potential against E/I for the saturation current a film was found whose thickness was such that both ratios were equal to unity. The nearest experimental approach to this critical thickness are the values cited in the above table.

Fig. 4 represents the conditions for film 4 in Table I. The units of the current axis are ten times larger than those for curves Figs. 2 and 3.

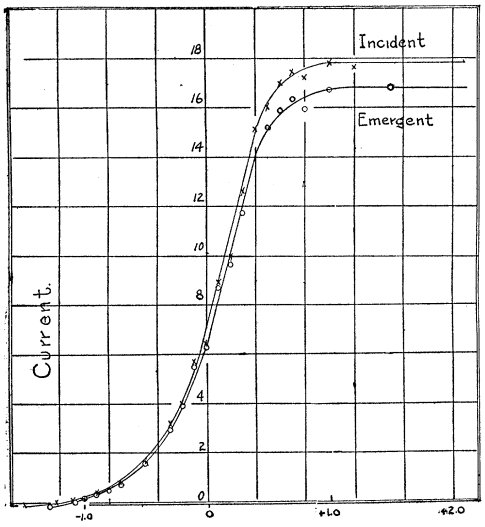

Fig. 4.

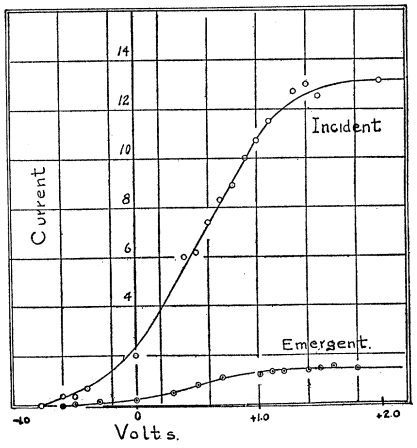

Fig. 5.

The incident velocities are now slightly larger than the emergent velocities. After this thickness the emergent velocities drop off faster than the incident, as seen in Fig. 5. This curve represents the conditions in a thick film. The emergent velocity curve is rapidly disappearing while the incident attains the normal value for platinum, equivalent to a film of infinite thickness.

DISCUSSION.

Evidently the most important results obtained are those from films whose thicknesses are less than 10^{-7} cm. Here both the ratios of emergent to incident velocity and current are greater than unity.

The current phenomena we have seen can partly be explained by Partzsch and Hallwachs' absorption curves, showing that the absorption for the emergent effect is greater than for incident effect, although the

[1] Loc. cit.

photo-electric current seems to be out of proportion to the absorption curves.

If the current effect were due to a layer of gas or double layer at the surface of the film, then this would effect thin films and thick films alike.[1]

Due to some secondary effect there may be a change in the coefficient of absorption of these thin films large enough to account for this sudden increase in current.

A view more in agreement with recent developments on the presence of "reactionsfähige gase" affecting the photo-electric current, would be the following. The relative difference between the observed photo-electric currents and the absorption curves as determined optically by Partzsch and Hallwachs, can be accounted for by the tremendous influence that various impurities in the residual gases, in which they were deposited, have on these films. S. Werner[2] has conclusively shown that platinum films deposited in various gases, although of equal thickness, possess very different photo-electric sensitiveness. They are also more sensitive than the metal itself.

At a thickness of 10^{-7} cm. the film may have special properties of occluding or absorbing the residual gases in which they are sputtered The photo-electric effect evidently depends upon these absorbed or occluded gases carried down with the particles of metal as they pass through the residual gases. For Hallwachs and Wiedman[3] have recently shown that the photo-electric effect of potassium could be obliterated by distilling the metal in vacuo, thus removing all intermolecular occluded or absorbed gases, while Kustner,[4] Fredenhagen[5] and Paech[6] have shown the importance of the presence of such gases to produce the well-known photo-electric effect of the various metals.

Since the photo-electric current is so largely influenced by the absorbed or occluded gases it might reasonably be concluded that the velocity of emission of the electrons is affected by these same conclusions. Because the above results show that a large increase in the photo-electric current is accompanied by a relative increase in the maximum velocity of emission.

Further experiments on other metals, using monochromatic light, are now under way. These we hope will throw more light on the diffi-

[1] O. Stuhlmann and K. T. Compton, loc. cit.

[2] S. Werner, Dissert. Uppsala, 1913; also Ark för Mat., Astron. Och. Fysik, 8, No. 27, S. 7, 1913.

[3] Wm. Hallwachs and G. Wiedmann, Ber. D. Phys. Ges., Jan., 1914, p. 107.

[4] H. Kustner, PHYS. Zs., XV (Jan.), p. 68, 1914.

[5] G. Paech., Ann. d. Phys., 43, p. 35, 1914.

[6] K. Fredenhagen, PHYS. Zs., XV (Jan.), 1914, p. 65.

culties underlying an explanation for the cause of the asymmetry in the velocities of emission.

I take great pleasure in acknowledging my indebtedness to Prof. A. W. Goodspeed, the director of the laboratory, for the generosity with which many special pieces of apparatus were purchased to complete this work.

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(To be continued.)