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THE RELATIONS OF THE PHOTO-POTENTIALS ASSUMED BY DIFFERENT METALS WHEN STIMULATED BY LIGHT OF A GIVEN FREQUENCY.

By A. E. Hennings and W. H. Kadesch.

It is the purpose of this investigation to examine the properties of a number of metals in respect to the maximum energies of photoelectrons emitted under the influence of light of several different frequencies. Nearly all investigators who have been engaged in photoelectric studies agree that such maximum energies exist, though Ramsauer[1] has obtained results which he considers conclusive evidence to the contrary. Professor Millikan, in a recent paper,[2] has given reasons for doubting the validity of Ramsauer's conclusion. The results herewith presented, as well as those of Millikan, Richardson and Compton, Hughes, and Kadesch, all lend support to Millikan's view.

A relationship between the maximum energies of emission of electrons from different metals acted upon by light of the same frequency has been sought by several observers, but it cannot be said that one has been definitely established. Page[3] has concluded from observations on three metals, aluminum, zinc and copper, that for a given frequency the same applied potential will in the case of each of the metals examined, just prevent the escape of electrons. His conclusion, however, is not as convincing as might be desired for the reason that effects due to reflected light render uncertain the exact potential at which the electrons ceased to escape. The data in Richardson and Compton's experiments[4] indicate that for a given wave-length the value of the apparent maximum energies of emission from six of the metals examined are all approximately the same. The differences observed seem to be no larger than might be

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[1] Ramsauer, Ann. der Physik, 45, p. 1121, 1914.

[2] Millikan, Phys. Rev., 7, p. 18, 1916.

[3] Page, Amer. Jour. Sci., 36, p. 501, 1913.

[4] Richardson and Compton, Phil. Mag., 24, p. 575, 1912.

accounted for by experimental uncertainties such as might be introduced, say, by variable surface conditions. Kadesch[1] using sodium and potassium and Millikan[2] using sodium and lithium, found it necessary however to apply potentials differing by as much as nearly one volt and over one half volt respectively to the illuminated plates in order to prevent the escape of electrons in the case of each of the wave-lengths used. This lack of concordance in results led Professor Millikan to suggest the present study.

APPARATUS AND EXPERIMENTAL PROCEDURE.

The photo-electric cell used in these experiments is the one designed and worked with three years ago by one of the authors in studying the relation between contact P.D.'s and photo-potentials. For a full description the reader is referred to the paper embodying the results of that investigation.[3] It will be sufficient in this place to state that the important feature of the cell is that eight metals are placed upon a wheel which, upon being rotated by means of an electromagnetic arrangement, brings the metals in succession into each of three positions. In one of these, the photo-potentials may be measured, in another the contact potentials, and in the third the surfaces of the metals may be renewed by means of a highly tempered steel scraper operated by a second electromagnet. When in the first position the metal place is opposite a Faraday cylinder of the form shown in Fig. 1. As is indicated, the inner gauze cylinder was connected to one pair of quadrants of an electrometer, the outer cylinder earthed, and the illuminated plate placed in communication with a potentiometer system by which the potentials applied to it were adjusted and read. The inner cylinder consisted of a double layer of fine meshed heavily oxidized copper wire netting. This blackened

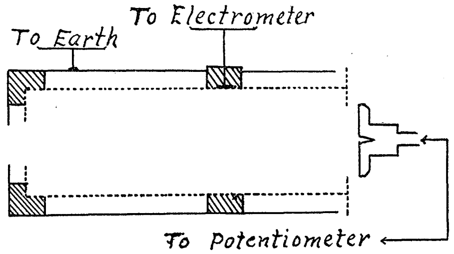

Fig. 1.

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[1] Kadesch, PHYS. REV., 3, p. 367, 1914.

[2] Millikan, PHYS. REV., 4, p. 73, 1914, and 6, p. 55, 1915.

[3] Hennings, PHYS. REV., 4, p. 228, 1914.

gauze was photo-electrically insensitive to wave-lengths at least as low as 2,302 Å.U. No effect due to reflected light could be detected in the case of any of the wave-lengths used.

The sensitiveness of the electrometer was about 1,400 divisions per volt. The electrostatic leak which at first was very troublesome because of the humidity during the summer months, was reduced to less than one division per minute by enclosing the photo-electric cell in a fairly tight earthed tin box, placing inside this box a tall wire-netting jar filled with calcium chloride, and forcing a stream of air already dried by passing over $CaCl_2$ into this drying jar, whence it escaped into the enclosing box.

The source of light was a mercury-in-quartz arc. A quartz lens of large aperture was used to concentrate a converging pencil of light upon the collimator slit of a quartz spectrometer. The quartz double prism was set to produce minimum deviation for wave-length 2,537 Å.U. The instrument was calibrated by means of the mercury spectrum. In adjusting the spectrometer for any desired wave-length the lines were identified by comparing the spectrum formed on a screen of uranium sulphate with a photograph of the mercury spectrum previously taken by means of the same spectrometer. Although the calibration was carefully made it was usually necessary in setting to make a slight readjustment in order to include as much as possible of the desired line in the slit of the telescope, and at the same time to make certain that wave-lengths shorter than the one desired were excluded. In making settings the collimator slit was made very narrow, but when the adjustment was completed the slit was opened to .5 mm. which was also the permanent width of the telescope slit. Since quartz lenses are not achromatic it was necessary to change the lengths of the collimator and telescope tubes for each new frequency. In order that the slit of the telescope might be at the same distance from the illuminated plate for all frequencies the spectrometer together with the mercury arc and quartz lens were so mounted that the whole system could be moved in a direction parallel to the axis of the telescope tube. The length of the collimator slit was limited by placing over it a metal screen with a horizontal opening 5 mm. wide. When adjustments were made in this way practically the whole of the surface of the metal disc was illuminated, with no light falling outside it.

The vacuum in the cell was the best obtainable. Before taking a set of observations the cocoanut charcoal bulbs attached to the system were heated to 400° C. for a couple of hours during which time a Gaede molecular pump was kept running. The bulbs were then allowed to cool, with the pump continuing to operate, and finally the system was closed off from the pump by a stop-cock. The carbon, thus freshened, would, when surrounded by liquid air, maintain a vacuum for two days so low that no indication of pressure could be observed with a McLeod gauge sensitive to less than .000002 mm. Mercury vapor was kept from entering the photo-cell proper by gold leaf, which, loosely packed between glass wool, filled a portion of the tube leading to the cell.

New surfaces were made in vacuo by scraping the electrodes as above described. Observations on the photo-currents were taken soon after the surfaces had been prepared. Since the photo-electric properties of metallic surfaces change with time the ages of the surfaces were noted when photo-currents were being measured.

The maximum energy of electrons emitted under illumination by a given wave-length was obtained by determining the point where the "distribution of velocity" curve cuts the voltage axis. It was not necessary to plot the complete curves since it was only with the portion near the voltage axis that we were concerned. It seemed desirable to plot the points representing current in terms of the saturation current taken as unity, as well as in terms of electrometer deflections. Accordingly measurements of the saturation current were made for each metal and each wave-length.

EXPERIMENTAL RESULTS.

Six metals, magnesium, aluminum, zinc, iron, tin and copper were studied, the maximum energies of emission of electrons being determined for light of various frequencies. The spectral lines employed were 2,302, 2,399, 2,537, 2,804, 3,132, 3,342, and 3,652 Å.U. The more electronegative metals are not sensitive to the longer waves. The results are graphically represented in Figs. 2 and 3, while Table I. gives the ages in vacuo of the surfaces at the time observations were made.

TABLE I.

Age of Metals in Hours.

Wave-length.	2302	2399	2537	2804	3132	3342
Magnesium	New	½	1–½	¼	New	New
Aluminium	1	1	1	¾	¼	¼
Zinc	1–¼	½	½	¼	¼	....
Iron	1	1	½	¼	....	....
Tin	2	1–½	1	¾	....	....
Copper	1–½	1–½	1–½	1	....	....

In obtaining the data from which the curves were plotted the procedure in general was to apply to the electrode smaller and smaller accelerating potentials or larger and larger retarding ones, and to observe the deflection of the electrometer needle, for each potential applied, due to illumination of the electrode for a chosen period of time. This was continued until the deflection had fallen to a small fraction of a division in a minute, or had become too small to be detected. The curves are so drawn as to give all points equal weight. In fact the points fell so regularly that with the relatively heavy lines drawn they are in almost every case covered by the curves. In some cases the observations were taken in the inverse order of that given above in order to determine the lower points of the curves with surfaces as new as possible, for it became apparent when this study was under way that the observed maximum energy of emission of electrons depends on age of surface. There is a shift with time which takes place at very different rates for different metals. It would have been desirable, if possible, to determine the emission velocities corresponding to zero age. There was an objection to making observations of photo-currents immediately after scraping, however, in the fact that in general the photo-sensitiveness changed very rapidly for a time, in some cases increasing, in others falling off. Under these conditions the photo-current-potential curves would everywhere have had too great or too small a slope, and the maximum electronic

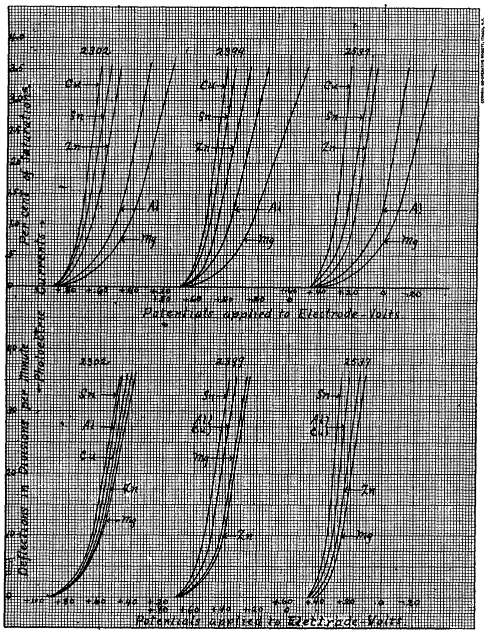

Fig. 2.

energy so determined might have been falsified accordingly. For these reasons the surfaces were not worked with until some little time after scraping. The age of each of the metals as given in Table I. is the mean age during the period of observation necessary to run the required portion of the distribution curve. That of magnesium is given as *new* in some cases. This means that the observations were begun as soon after the new surface had been formed as could be conveniently done, and moreover the lower points of the curve were located first.

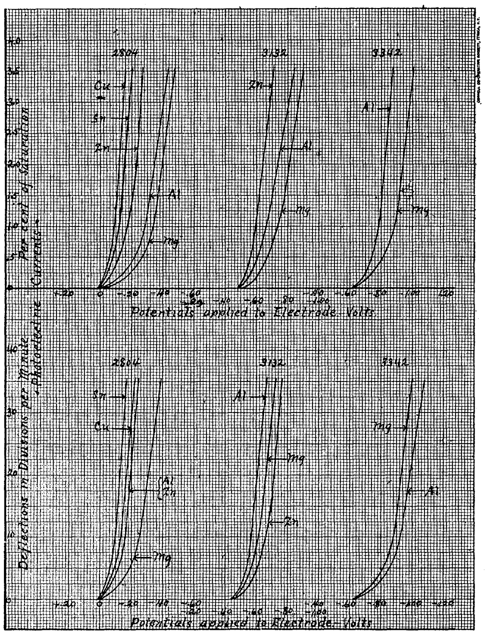

Fig. 3.

An examination of the curves in Figs. 2 and 3 shows that, when the currents are plotted as per cents. of the saturation current, they appear to emerge from a common point for each wave-length and spread out in a fan-like figure taking a definite order, viz., that of the contact potential series. In the case of the more electropositive metals the curves, on the scale here used, approach the voltage axis so gradually that it cannot be determined just where they run into it. While the curves plotted in this way show the true relation between the metals, they do not serve as well for determining the maximum retarding potentials as do those obtained by plotting the photo-currents in terms of the electrometer deflections observed in a chosen unit of time. When plotted in the latter way the curves for the electropositive metals plunge more sharply into the axis. The order now taken by the metals is not the same as before, and is different for different wave-lengths. There is no doubt that the curves meet the axis at a finite angle, and for a given wave-length at very nearly the same point. Curves are shown for only five of the six metals examined. Those for iron were omitted for the reason that, its contact P.D. differing but little from that of tin, the two curves would very nearly coincide.

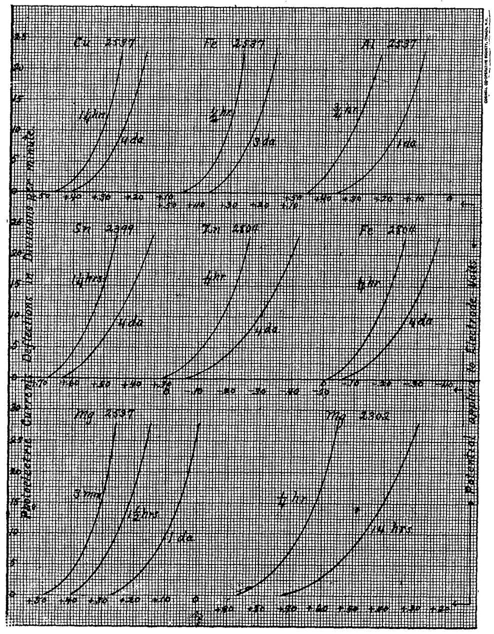

Fig. 4.

It has been noted that the age of the surface is to be taken into account. By starting observations immediately after scraping, and working very fast, a slightly greater apparent energy of emission was found for Mg and Al than for the other metals. On the other hand the curves for magnesium would have all met the axis to the right of the points for the other metals if it had been examined at an age as great as some of theirs. This is to be observed in Fig. 2 for wave-length 2,537 Å.U. in which case the magnesium surface was $1\frac{1}{2}$ hours old. Fig. 4 shows how the observed maximum energies of emission of electrons shift with age of surface. Specimen curves are given for the same metal with a number of wave-lengths and also for a number of metals with the same wave-length. It is seen that this sort of change is not peculiar to any metal or to any wave-length, but is a general phenomenon. How it may be accounted for will be considered later.

THEORETICAL CONSIDERATIONS.

The general form of Einstein's equation

$$\tfrac{1}{2}mv^2 = Ve = h\nu - p \qquad (1)$$

may be rewritten following Professor Millikan's notation

$$\tfrac{1}{2}mv^2 = Ve = h\nu - (p_1 + p_2) \qquad (2)$$

where

p_1 = work to detach electron from mother atom

p_2 = work to liberate the "free" atom from the metal surface.

The energy which just suffices to detach and set free an electron may be determined by observing the greatest wave-length to which the metallic surface is photo-sensitive. If ν_0 is this critical frequency at which electrons cease to be emitted, it follows from (2) that

$$h\nu_0 = p_1 + p_2. \qquad (3)$$

The *observed* maximum energy of emission due to any given wave-length may be found by measuring either the positive potential acquired by the emittor, or the positive potential which must be applied to it, just to prevent the escape of electrons, in the presence of a Faraday cylinder the inner surface of which opposes that of the emittor. If the Faraday cylinder is electronegative with respect to the illuminated surface, the escaping electron has initially an energy greater than that corresponding to the potential observed as above. Hence, denoting by V_0, the observed maximum positive potential, and by K the contact P.D. between the opposing surfaces, we may write in view of (2) and (3)

$$(V_0 + K)e = h\nu - h\nu_0. \qquad (4)$$

For another emittor excited by light of the same frequency and discharging electrons into the same Faraday cylinder

$$(V_0' + K')e = h\nu - h\nu_0'. \qquad (5)$$

If the second emittor be the more electro-positive its potential is the higher by $K' - K$. Designating this as the contact P.D. between the two emittors, we find by subtracting (4) and (5) that

$$\text{Contact P.D.} = \frac{h}{e}(\nu_0 - \nu_0') + (V_0 + V_0'). \qquad (6)$$

The way in which e has been introduced into the preceding equations takes care of the negative character of the electronic charge so that in this final equation h/e is to be taken as a positive ratio.

For freshly scraped surfaces, the V_0's agree so closely for all of the six metals studied that the relation

$$\text{Contact P.D.} = \frac{h}{e}(\nu_0 - \nu_0') \tag{7}$$

might well seem a general one. This is indicated also by the observations of Richardson and Compton, and those of Page. The wide differences between the apparent maximum electronic velocities observed in the experiments of Millikan and of Kadesch referred to above suggest however that this relation probably exists only for the ordinary metals.

In deducing equations (6) and (7) it was tacitly assumed that the surfaces were homogeneous, and in a steady condition; conductors, but not necessarily metallic. If films form rapidly upon surfaces thus freshly made in vacuo, and there is reason for believing that they do, then new factors are introduced which must be taken into account in interpreting the relation between the observed V_0's.

Attention has been called to the change in the apparent maximum velocity of emission of electrons with age of surface. In order to conceive a mechanism by which this change might be brought about, let us assume that a metallic surface, prepared as in these experiments in the best of vacua, does become coated with a film. Assume that this gradually increases in thickness, that it is at least partially transparent but photo-electrically insensitive to the light employed, that it does not affect the contact P.D. between electrode and Faraday cylinder, and that electrons passing through it suffer a loss in energy, which increases with increasing thickness of the film. In the presence of such a film the electron requires an additional amount of energy just to free itself. If we call this p_3, the minimum initial energy which the escaping electron must have is equal to $p_1 + p_2 + p_3$, instead of $p_1 + p_2$, and the potential necessary to prevent electrons from reaching the Faraday cylinder is equal to $V_0 - p_3/e$, instead of V_0 as in (4). Hence denoting this potential by V_0'' we have for a film coated surface

$$(V_0'' + K)e = h\nu - (p_1 + p_2 + p_3). \tag{8}$$

From this relation it is seen that as p_3 increases, V_0'' decreases. Thus a gradual shift of the photo-current-potential curves toward smaller retarding potentials may be accounted for by the formation of a film which is increasing in thickness. If the film have only the properties assumed for it above and it began forming at isolated points, spreading out from these until the entire surface were overspread, the shift would begin only when the metal became completely covered.

It is generally believed that gas films do form under the conditions mentioned above. The properties assumed for them are just such as we should expect them to have except that perhaps they might be supposed to alter the contact P.D. between electrode and Faraday cylinder. That this would not necessarily be the case was shown by testing the effect of sheets of non-conductors on the contact P.D. when placed between an old copper surface and one of freshly polished aluminum. The contact P.D. between these surfaces in air was .87 volt. With sheets of mica and paper, and a plate of glass placed successively between, it was .91, .77 and .86 volt respectively. On repeating the observations, values slightly higher or lower than that obtained without the non-conducting sheets were found. These fluctuations were due no doubt to electrical charges on the insulators which could not be completely eliminated. We assume therefore that a gas film would probably not affect the actual contact P.D. and would not give rise to apparent fluctuation in its value, because, owing to the intimate contact between film and electrode, no residual charges would be likely to be held. It might, however, absorb energy from the electrons emitted from the underlying metal.

In addition to the inactive film assumed above it may be that others are formed which not only are photo-sensitive to light of frequencies within the range usually employed, but which also show a contact P.D. with reference to both the Faraday cylinder and the metal of which the electrode is made. If such a film exists, and is formed as we have assumed the other to be by starting at isolated points, then as long as the metal had not become completely covered there would be a non-homogeneous surface. The measured contact P.D. between this surface and any other old enough to have come to a steady condition would change progressively from that corresponding to all metal to that corresponding to all film.

How such a film would affect the potential to be supplied to the electrode in order just to prevent the escape of electrons it would be impossible, since the question as to the nature and origin of contact P.D.'s is still unanswered, to say. If these have their rise in the surfaces of the opposed conductors, depending only upon the nature of those surfaces, and being unaffected by the presence in the immediate neighborhood of other surfaces of different character then the mottling and ultimate overspreading of a metallic surface by an active film might have any one of three effects, depending upon the nature of metal and of film. If equations (4) and (5) represent the conditions for homogeneous surfaces, of film and metal respectively, and if V_0 were greater than V_0' then the potential to be applied would rise abruptly from V_0' to V_0 on the appearance of the first bit of film. If V_0 were equal to V_0' then the formation of such a film would leave the applied potential unchanged. If V_0' were the greater, then this potential would remain unaltered until the last bit of metallic surface were covered, when an abrupt fall from V_0' to V_0 would occur.

If, on the other hand, the velocity of escape of electrons from one surface or surface element to another is affected by the presence in the near proximity of one of them, of surfaces or surface elements of a different sort, then it is possible that the potential to be applied in order just to prevent the escape of electrons from one of the component portions of a composite surface may not be at all the same as that required to prevent their escape from a surface made up entirely of this component. From the established relations of contact P.D.'s between complex surfaces it may be shown that an initially homogeneous surface upon which a film electronegative to it is forming might discharge electrons with abnormally high velocities, while the electronegative film, in the earlier stages of its formation, might discharge them with abnormally low velocities.

Although it has not been demonstrated that active films come into play in precisely the manner above postulated, there at least seems to be evidence that such exist. In the case of tin the photo-currents increased very markedly for a time after scraping, often after an hour or two reaching a maximum value as much as three times that observed immediately after the surface was made. A similar effect was noted with aluminum and zinc when the stimulating light frequency approached that of the long wave-length limit for these metals. This phenomenon has also been observed by Millikan and Souder[1] in working with the more electropositive metals. In their experiments it was even more marked than here. The falling off of the photo-currents and a subsequent change in the value of the maximum energy of emission may be due, at least in part, to the formation upon the active film of an inactive one of the sort assumed above.

Summary.

The photo-current-potential curves obtained in these experiments plunge sharply into the potential axis. This indicates that photo-electrons released from a given surface under the influence of light of a given frequency have energies which do not exceed a definite finite value.

The apparent maximum positive potentials assumed by six of the common metals under the influence of light of a given frequency were the same, almost to within the limits of error of observation, so long as the surfaces had been newly scraped in vacuo. The contact P.D. between any two of these is therefore equal, to the same approximation to

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[1] Millikan and Souder, Phys. Rev., 4, p. 73, 1914.

$$\frac{h}{e}(\nu_0' - \nu_0'').$$

A falling off in the maximum energy of emission of electrons was observed with increasing age of surface. This was most marked in the case of magnesium but took place to a smaller degree with all the other metals. This shift can be explained on the assumption of the gradual formation of retarding films.

In conclusion, we wish to acknowledge our indebtedness to Professor Millikan for placing at our disposal the resources of Ryerson Laboratory, and for offering valuable suggestions as the work progressed.

The University of Chicago.