LIGHT SENSITIVITY OF CUPROUS OXIDE AND OF SELENIUM

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Abstract

Three photo-electric effects for certain samples of Cu_2O and Se as functions of wave-length.—Light from a tungsten lamp or iron arc was dispersed by a quartz spectrometer. Measurements with a thermocouple enabled all results to be reduced to unit light intensity. The observations agree well with previous results obtained with various samples. (1) *Decrease of resistance* was measured for the range 3900 to 6000 A for Cu_2O, maximum at 4600 A, and for 4300 to 9300 A for Se, maximum at 7000 A. (2) *Photo-electrolytic potential* was found to exist for both back (contact with air) and front (contact with distilled water) illumination, and was measured in the case of front illumination for the range 2700 to 5500 A for Cu_2O (maximum at 3500 A, upper limit about 5600 A), and for 2700 to 9000 A for Se (maximum at 5700 A, upper limit about 9500 A). The effect was positive and proportional to the intensity I for Cu_2O and to $I^{\frac{2}{3}}$ for Se. (3) *Photo-electric wave-length limit* was found by the use of absorption screens to be at about 2570 A for Cu_2O and at 2260 A for Se. For both Cu_2O and Se, all samples showed the same photo-electric limits and those which showed a change of resistance also showed the photo-electrolytic effect, but not vice-versa.

Introduction

In the present investigation, three photo-effects have been measured on the same sample, since different samples have been found to vary greatly in their sensitivity. The photo-effects that have been measured are: first, the change in the electrical resistance produced by light; second, the change in the potential of the substance produced by light when the substance is one of the plates in an electrolytic cell, i.e. the photo-electrolytic effect; and third, the photo-electric effect.

Apparatus and Method

For determining the change in the electrical resistance produced by wave-lengths 6000 to 4000 A for Cu_2O, and 9000 to 4000 A for Se, a quartz spectrometer, as described by A. H. Pfund,[1] was used. The source of light was a tungsten lamp of 32 c.p. A water cell was inserted to cut out the strong heat rays. An orange glass screen was used as a shutter for wave-lengths shorter than 4650 A, to reduce the effect of scattered light.

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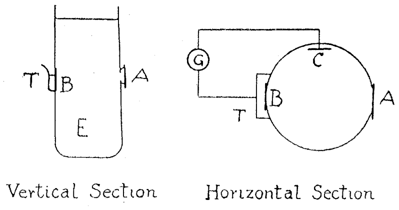
[1] A. H. Pfund, Phys. Rev. **7**, 289, 1916

In measuring the change of resistance produced by different wavelengths of light, the Wheatstone's bridge was balanced as closely as possible with the resistance cell, not illuminated, as the unknown resistance. The reading of the galvanometer was taken. Then, by means of the spectrometer, a small region of the spectrum was allowed to fall on the substance, and the steady deflection of the galvanometer was read. The change of resistance was found to be independent of the length of time of illumination, unless that time was exceedingly short. The difference between these galvanometer readings was proportional to the change of resistance of the substance illuminated, as it was experimentally proved that for the galvanometer and resistances used, the deflection was proportional to the change of resistance in one arm of the bridge, the change being small in comparison to the total resistance. The substance being investigated was then replaced by a thermocouple connected to another galvanometer, and the relative intensity of the different portions of the spectrum was obtained. Pfund[1] in his investigations on Cu_2O and Nicholson[2] in his investigations on Se, showed that for any monochromatic portion of the spectrum for which the light is not transmitted by the substance, the change in resistance is porportional to the square root of the intensity of the incident light. Using this fact, the change in resistance produced by equal light intensities of the various regions of the spectrum was obtained.

For determining the photo-electrolytic effect produced by the different regions of the spectrum in the range 8700 to 2500 A, the same quartz spectrometer was used, but the source of light was an iron arc. The substance to be investigated was sealed into the side of the glass cell, as shown at B in Fig. 1, opposite a quartz window A. Great difficulty was experienced in obtaining a good electrical contact to B, but this was finally overcome by sealing a small copper sheet T directly behind B, and filling the space between the copper and B with mercury. The other electrode of the cell was in some cases a sample of the same substance as



Vertical Section Horizontal Section

Fig. 1. Photoelectrolytic cell.

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[2] P. J. Nicholson, Phys. Rev. 3, 1, 1914

B, sealed into the side of the tube in such a position that the light could not reach it; in other cases a platinum wire or zinc strip immersed in the solution. The solution E was distilled water when working with Cu_2O, whereas a few drops of nitric acid were added to the distilled water when working with Se. The two electrodes were joined to the terminals of a high resistance galvanometer g.

In measuring the photo-electrolytic effect as a function of wave-length the cell was exposed to the different regions of the spectrum by the quartz spectrometer, and the corresponding throws of the galvanometer were obtained. These throws were porportional to the change in potential produced in the substance. The thermocouple replaced the electrolytic cell after each reading and thus the relative intensities of the incident light at each reading were determined.

To determine the relation between the change in potential produced, and the intensity of the source, the unresolved radiations of a 32 c.p. tungsten lamp was focussed on the specimen. By means of a rotating sector, the intensity was reduced consecutively to ½, ¼ and ⅛ of its total intensity, and the corresponding changes in potential were noted by the galvanometer readings. The results are given in Table I.

TABLE I

Change of potential as a function of intensity of the source

Relative intensity I	Cu_2O dp(obs.)	Cu_2O dp/I	Se dp(obs.)	Se $dp/I^{\frac{2}{3}}$
1	20	20	48.3	48.3
½	10.05	20.1	32.2	51.1
¼	5.2	20.8	23.85	60.1
⅛	2.7	21.6	14.86	59.4

It was shown that for the unresolved radiation, the change in potential produced is proportional to the intensity of the radiation in the case of Cu_2O, and is proportional to the two-thirds power of the intensity in the case of Se. It is assumed that the same law holds for the monochromatic radiations that are not transmitted by the substance. Using this relation, the change in potential produced by equal light intensities of the various regions of the spectrum was obtained.

The apparatus used for determining the longest wave-length that will cause a photo-electric effect of the substance is indicated in Fig. 2. The photo-electric cell was enclosed in an earthed tin case, which was connected by a brass pipe to the brass case containing the electrometer. A small hole was cut in the tin case to allow the light to fall on the cell. The source of light was an aluminium spark when working with Cu_2O, and an iron arc when working with Se. This light was focussed on the substance in the cell by means of a quartz lens. In determining the long wave-length limit that will cause the photo-electric effect, screens of various thicknesses of glass were used, and when that screen was found which would give a very small deflection of the highly sensitive electrometer, the transmission spectrum of that screen was taken and the shortest wave-length that it transmitted was the longest wave-length that would cause the photo-electric effect of the substance.

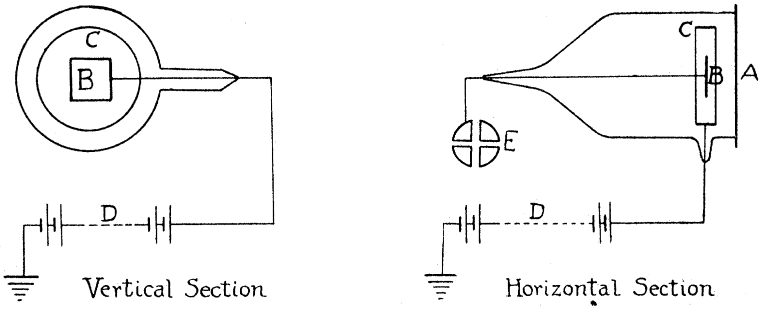

Fig. 2. Photo-electric cell. *A*—Quartz window; *B*—Cu_2O or Se; *C*—Copper cylinder; *D*—Battery of 112 volts; *E*—Electrometer.

Results for Cuprous Oxide

The observed change of resistance of Cu_2O produced by radiations of different wave-lengths in the region 6000 to 3900 A was in good accord with the work done by A. H. Pfund.[1] The final results are shown in Curve I, Fig. 3 in which the ratio of the change of resistance to the square-root of the relative intensity of the radiation is plotted against the corresponding wave-length of light. It will be noted in the graph that there is a slight maximum at 4600 A.

The effect of wave-length on the change of potential of the Cu_2O in an electrolytic cell had been observed by Pfund and E. Karrer, but the results were never published. The readings taken in this investigation confirm their results. They are shown in Fig. 4 in which the change of potential is plotted against the corresponding wave-length in Curve I, and the ratio of the change of potential to the relative intensity is plotted against the corresponding wave-length in Curve II. It will be noted in Curve II that there is a maximum effect at about 3500 A, and that the effect continues throughout the ultra-violet to 2600 A, that is, as far as was investigated.

This potential effect was also observed when the back of the Cu_2O plate was illuminated, that is, when the light did not pass through the electrolyte, but fell on that face of the Cu_2O plate which was in contact with the air. Stray light was excluded from the front face, and the sample was opaque to all rays except the red.

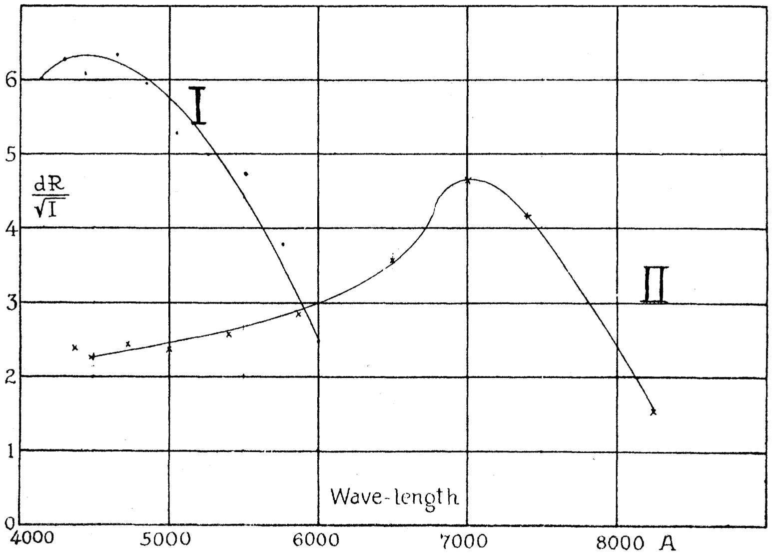

Fig. 3. Change of resistance of Cu_2O (I) and of Se (II) for light of various wave-lengths.

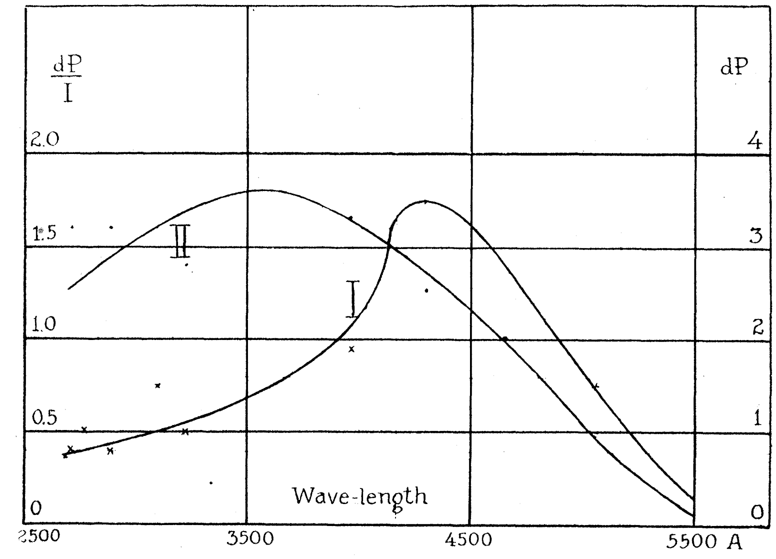

Fig. 4. Change of potential of Cu_2O (I) and Se (II) in an electrolytic cell for light of various wave-lengths.

The absolute magnitude of the potential effect, for front illumination, was determined by connecting the galvanometer to a potentiometer. It was found that the change of potential produced by 3500 A of intensity as obtained from the iron arc, was of the order of magnitude of 10^{-5} volts.

T. W. Case[3] has investigated the effect of light on one electrode of a cuprous oxide voltameter, with copper formate as the electrolyte. In the unresolved radiation of sunlight, he obtained 0.11 volts for the full intensity. But in his work he found that the illuminated Cu_2O plate has its potential lowered. In the present investigation, the illuminated Cu_2O plate was made positive as the result of illumination, the current flowing from the plate to the dark electrode through the external circuit.

R. A. Millikan[4] records the long wave-length limit for copper oxide to be 2535 A with a possible error of 50 A. The long wave-length limit as obtained in the present investigation was 2572 A.

Three pieces of Cu_2O were investigated. They showed the same long wave-length limit for the photo-electric effect, and the same characteristic photo-electrolytic action; but, even though a particular specimen showed a large photo-electrolytic action, it did not, in two cases, show a measurable change of resistance with exposure to light. The mode of preparation of the Cu_2O samples was that described by A. H. Pfund.[1]

Results for Selenium

The observed changes of resistance of Se produced by radiation in different regions of the spectrum in the range of 9000 to 4000 A are in good accord with the results obtained by Nicholson.[2] The final results are shown in Curve II, Fig. 3 in which the ratio of the change of resistance to the square-root of the relative intensity of the radiation is plotted against the corresponding wave-length of light. It will be noted in the graph that there is a sharp maximum at 7000 A.

The change of potential of the Se in an electrolytic cell when the other electrode is platinum has been observed by Minchin.[5] In the present investigation a very much larger effect was observed when the other electrode was a strip of zinc; but this was probably due to the smaller internal resistance of the cell when the large zinc electrode was used. The results for a cell with Se and Zn as electrodes, in distilled water with a few drops of nitric acid added, are recorded in Fig. 5. Curve I shows the relation of the change of potential to the corresponding wave-lengths. Curve II shows the relation of the ratio of the change of potential divided

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[3] T. W. Case, Am. Electrochem. Soc. Trans. **31,** 351, 1917

[4] R. A. Millikan, Phys. Rev. **7,** 18, 1916

[5] J. M. Minchin, Phil. Mag. (5) **21,** 207, 1891

by the two-thirds power of the relative intensity of the radiation to the corresponding wave-lengths. Care was taken that the light did not fall on the zinc. The direction of the current obtained was from the illuminated Se to the dark electrode through the external circuit, that is, the Se is raised to a higher potential, by the action of the light. It will be noted from Curve II that there is a decided maximum at about 5700 A.

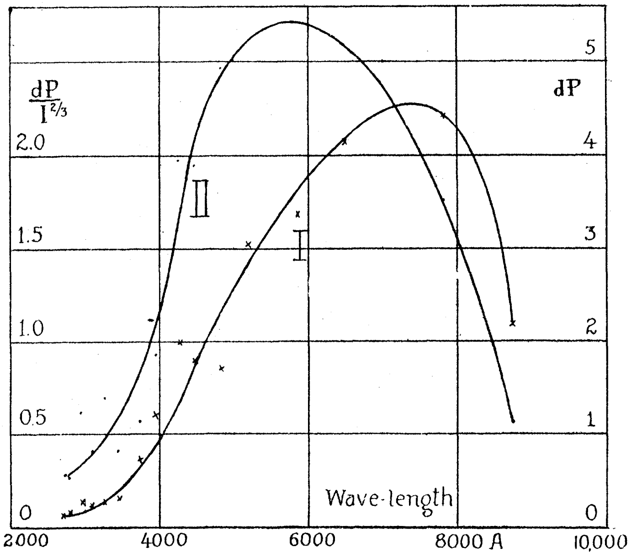

Fig. 5. Change of potential of Se in an electrolytic cell with Zn as the other electrode. Curve I gives dP; Curve II, $dP/I^{2/3}$.

The long wave-length limit as obtained for Se was 2260 A.

Three pieces of Se were investigated. They showed the same long wave-length limit for the photo-electric effect, and the same characteristic photo-electrolytic action, but although the three specimens showed a large photo-electrolytic action, only one showed a measurable change of resistance with exposure to light. The mode of preparation of the Se samples was that described by A. H. Pfund.[6]

Discussion

It has been the purpose of this paper to observe the above-mentioned three photo-effects on the same sample, with a view to aiding in the theoretical interpretation of these and other experimental facts.

The fact that for both Cu_2O and Se, the resistance effect, the photo-electrolytic effect, and the photo-electric effect begin at increasingly short wave-lengths in the order mentioned, indicates (1) that least

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[6] A. H. Pfund. Phys. Rev. **28**, 324, 1909

energy is required to simply excite the electrons (assuming Thomson's doublet theory of resistance, since it was found to explain some of the experiments of A. H. Pfund),[1] (2) that a greater amount of energy is required to remove an electron from the substance, and (3) that the greater the dielectric constant of the medium surrounding the substance the less the amount of energy necessary to remove the electron. It is of interest to note that the photo-electric effect of Cu_2O begins at approximately 2570 A and that the ratio $-dR/\sqrt{I}$ begins to decrease at approximately 2800 A (according to Pfund's[1] work in the ultra-violet), having been steadily increasing up to this point. That these two effects should occur at the same wave-length is what would be expected on Thomson's doublet theory of resistance, due to electrons being ejected completely from the substance.

In conclusion, I desire to express my appreciation to Professor Ames and to the entire graduate Physics department of the Johns Hopkins University for the interest taken in the work and to William H. Crew for making the diagrams. I especially want to thank Dr. Pfund, who suggested the problem and so cheerfully aided me in every way.

Johns Hopkins University,
May, 1923.