

# VARIOUS PHOTO-ELECTRICAL INVESTIGATIONS.

By W. W. Coblenz.

---

## ABSTRACT.

In this paper are given miscellaneous data which were obtained in connection with the general investigation of photoelectrical sensitivity.

Data are given upon: (1) the photo-electrical sensitivity of artificial preparations of molybdenum sulphide, (2) the effect of heat and electrical treatment upon the photo-electrical sensitivity of molybdenite and stibnite, (3) the photo-electrical sensitivity of various artificial preparations, (4) the positive and negative photo-electrical reaction in molybdenite, (5) the photo-electrical sensitivity of molybdenite and stibnite in the extreme ultra-violet, (6) the spectral response curves of Case's barium and strontium photo-electric cells, (7) the spectrophoto-electrical reaction curves of cuprous oxide and of lead antimony sulphide, (8) the spectrophoto-electrical sensitivity of iodine, and (9) spectroscopic and chemical analyses of photosensitive and nonsensitive molybdenite.

---

## CONTENTS.

	Page.
I. Introduction.....	586
II. Methods of testing the photosensitivity.....	587
III. Effect of heat treatment upon the photo-electrical sensitivity of molybdenite and stibnite.....	587
1. Molybdenite.....	587
2. Stibnite.....	588
IV. Effect of electrical treatment upon the photo-electrical sensitivity of molybdenite and stibnite.....	590
1. Molybdenite.....	591
2. Stibnite.....	591
V. Artificial preparations.....	592
1. Dry process preparation of $\text{MoS}_2$ .....	592
(a) Methods of mounting and testing.....	592
(b) Results.....	593
2. Wet process preparation of $\text{MoS}_3$ and $\text{MoS}_2$ .....	594
(a) Results.....	594
3. Experiments on mixtures with $\text{MoS}_2$ .....	594
4. Miscellaneous preparations.....	595
VI. Spectroscopic and chemical analysis of molybdenite.....	597
1. Spectroscopic analysis.....	597
2. Chemical analysis.....	597
VII. Photopositive and photonegative reactions in molybdenite.....	598
1. Effect of intensity on the photonegative reaction.....	599
2. An equal response to equal energy spectrum.....	600

	Page.
VIII. Photo-electrical sensitivity of molybdenite and stibnite in the ultra-violet spectrum . . . . .	601 602
IX. Spectral response curves of Case's barium and strontium photo-electric cells	
X. Spectrophoto-electrical sensitivity of cuprous oxide and of lead-antimony sulphide . . . . .	603
1. Cuprous oxide . . . . .	603
2. Lead-antimony sulphide . . . . .	604
(a) Boulangerite and jamesonite . . . . .	604
XI. Spectrophoto-electrical sensitivity of iodine . . . . .	605
XII. Summary . . . . .	606

## I. INTRODUCTION.

The purpose of this paper is to give miscellaneous data which were obtained in connection with the general investigation<sup>1</sup> of the photo-electrical sensitivity in various substances, but not heretofore published. Some of the data were obtained in connection with a research problem conducted in cooperation with the Signal Corps of the War Department.

Samples of the mineral molybdenite ( $\text{MoS}_2$ ) obtained from different localities can be divided into two classes which have widely different physical characteristics: *Class 1* has a low specific electrical resistance which at room temperatures is not affected to an appreciable extent when exposed to thermal radiation of various wave lengths. Only at low (liquid air) temperatures is there any indication of photo-electrical sensitivity; *class 2* has a high specific resistance, and some samples have small regions which decrease greatly in electrical resistance when exposed to thermal radiations of different wave lengths. Moreover, this spectrophoto-electrical sensitivity is greatly increased at low temperatures.

In view of these facts it was deemed desirable to prepare artificial material and subject it (as well as the natural mineral) to heat and pressure treatment such as may have occurred in nature. Moreover, since the photosensitivity is usually localized in spots, it was deemed desirable to prepare samples of the various known sulphides of molybdenum to determine whether they contribute to or cause the photosensitivity in  $\text{MoS}_2$ .

---

<sup>1</sup> General survey: Bismuthinite, B. S. Sci. Papers, No. 322; Molybdenite, B. S. Sci. Papers, No. 338; Silver sulphide, B. S. Sci. Papers, No. 344; Thalofide, B. S. Sci. Papers, No. 380; Positive and negative conductivity phenomena, B. S. Sci. Papers, No. 398; Proustite, B. S. Sci. Papers, No. 412; Argentite, B. S. Sci. Papers, No. 446; Bournonite and Pyrrargyrite, B. S. Sci. Papers, No. 451.

## II. METHODS OF TESTING THE PHOTSENSITIVITY.

In order to test the photo-electrical sensitivity the material under examination was connected with a dry battery and a galvanometer. A vacuum tungsten lamp at a fixed distance from the sample was used as a standard source of radiation. The substance to be tested is usually a poor electrical conductor, and when it is connected through an electrical battery there is a galvanometer deflection caused by the "*dark current*." On exposing the substance to the total radiation from the standard lamp, if it is photo-electrically sensitive there is an additional deflection of the galvanometer caused by the "*light current*." The ratio of the *light current* to the *dark current* is a measure of the photo-electrical sensitivity, or of the "*photo-electrical efficiency*" as used in this paper. It is, of course, arbitrary, since it depends upon the intensity and the distance of the light stimulus from the sample. But since these two factors were kept constant this method of comparing the photo-electrical sensitivity of different substances was satisfactory.

## III. EFFECT OF HEAT TREATMENT UPON THE PHOTO-ELECTRICAL SENSITIVITY OF MOLYBDENITE AND STIBNITE.

In previous papers it was shown that on raising the temperature of molybdenite (to about  $100^{\circ}$  C.) the photo-electrical sensitivity is greatly decreased, but is again restored on cooling to room temperature. The present data relate to the effect of prolonged heating upon the photosensitivity of the minerals molybdenite and stibnite.

### 1. MOLYBDENITE.

It is well known that the photo-electrical sensitivity of selenium is brought about by heat treatment at the proper temperature. It was, therefore, of interest to make similar tests upon various samples of molybdenite, especially since it is not known what temperature changes the natural mineral may have undergone.

The first tests consisted in heating a sample of molybdenite to a low red for a moment by passing an electrical current through it. Starting with a sample of  $\text{MoS}_2$  which was photosensitive, it was found that heating it to  $700^{\circ}$  C. for a short time destroyed the sensitivity. A similar heat treatment of nonsensitive samples of  $\text{MoS}_2$  did not render them sensitive.



In another test, a sample of photosensitive  $\text{MoS}_2$  was heated to a low red on a metal plate till it had become covered with white oxide. After standing for 24 hours and after peeling off the oxide, the intrinsic photo-electrical sensitivity (ratio of light current : dark current) was practically the same (30 per cent) as that of the unheated sample.

In the third test seven samples of  $\text{MoS}_2$ , which were photosensitive before heating, were placed in an inclosed electrically heated porcelain tube and kept for one hour at each of the following temperatures: 120, 200, 300, 400, 500, and  $640^\circ\text{C}$ . After each heating they were clamped into a suitable mounting and tested for photosensitivity. For the temperature range up to and including  $400^\circ\text{C}$ . no systematic change in photosensitivity (either increase or decrease) was observed. At  $500^\circ\text{C}$ . the samples became oxidized (and apparently less sensitive), and at  $640^\circ\text{C}$ . they were destroyed by oxidation.

In the fourth test of three photosensitive samples of molybdenite, which were heated for a short time at  $550^\circ\text{C}$ . and then at  $600^\circ\text{C}$ ., it seemed that the intrinsic sensitivity was considerably decreased from that of the unheated material.

Finally, four sensitive samples of molybdenite were heated at  $600^\circ\text{C}$ . for a short time. After scraping off the oxide, the average intrinsic sensitivity was found to have decreased about 50 per cent.

The conclusion to be drawn from these tests is that slow-heat treatment has no marked or permanent effect upon the intrinsic photo-electrical sensitivity of molybdenite in the temperature range up to  $500^\circ\text{C}$ . At temperatures somewhat above  $600^\circ\text{C}$ . the sensitivity appears to be permanently decreased. Raising the temperature to a low red (about  $700^\circ\text{C}$ .) destroyed the photosensitivity.

## 2. STIBNITE.

In previous tests by Jaeger <sup>2</sup> and by the writer it was found that, on melting stibnite on an iron plate and allowing it to solidify, the photo-electrical sensitivity was destroyed. Jaeger found the specific resistance of the resolidified material several thousand times smaller than that of the natural crystal.

On the other hand, in an extended research Olie and Kruyt <sup>3</sup> sometimes succeeded in melting and resolidifying stibnite without destroying its photo-electrical sensitivity. They prepared artificial stibnite, sometimes in open tubes (also in evacuated tubes

<sup>2</sup> Jaeger, *Zs., für Kristallographie*, 44, p. 45; 1907.

<sup>3</sup> Olie and Kruyt, <sup>3</sup> *Koninklijke Akademie Von Wetenschappen, Amsterdam*, 14, p. 740; 1912.

heated to  $600^{\circ}$  C.), and found that the highest photo-electrical sensitivity was obtained when the Sb and S were mixed in exact proportions to give  $Sb_2S_3$ . They thought that the photo-electrical sensitivity was affected by the kind of glass tubes used in preparing the material. Using a different kind of glass, they did not obtain a single preparation which was photosensitive. By performing the operation in evacuated glass tubes they succeeded in remelting the native (Japanese) stibnite without destroying its photo-electrical sensitivity. A loss of 0.5 per cent of S resulted in a totally inert preparation.

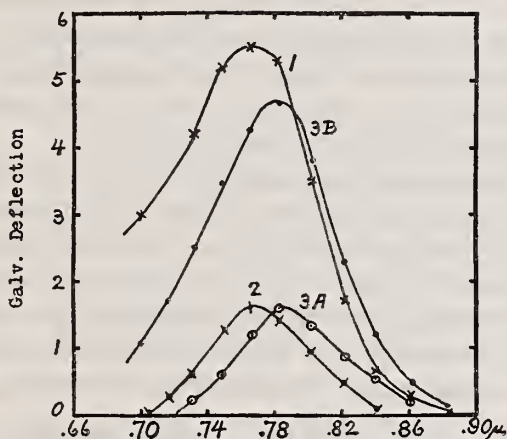


FIG. 1.—Effect of heating upon the spectrophotoc-electrical sensitivity of stibnite.

In the present tests two samples of stibnite which were found sensitive were heated in an electric furnace for one hour at each of the following temperatures: 120, 200, 300, and  $400^{\circ}$  C., after which the samples were cooled and their photosensitivity determined. The average intrinsic photosensitivity (ratio of light current : dark current) as determined after heating to these temperatures did not change systematically in the temperature interval up to  $400^{\circ}$  C. At  $500^{\circ}$  C. these crystals were completely oxidized by the long heating.

In another test, four samples were heated to  $500^{\circ}$  C. for a short time when they were found to have melted and merged into two lumps, one of which appeared porous and was nonsensitive photo-electrically. The other lump was as photosensitive as the original unmelted material. On examination under a low-power microscope it was found that this photosensitive lump was recrystallized,

the surface being covered with patches of acicular crystals. Its size was 12 by 4 by 2.5 mm.

In order to compare the spectrophoto-electrical sensitivity curve of this recrystallized sample with that of the unmelted material, electrodes were provided which consisted of copper wires, the ends of which were melted into beads, which, in their molten state, were pressed into the stibnite. Contrary to the unsatisfactory experience with silver sulphide,<sup>4</sup> this method of attaching the electrodes did not introduce an unsteadiness (presumably as a result of electrolysis) in the dark current.

In Figure 1, curves 1 and 2 depict the spectrophoto-electrical sensitivity (for an equal energy spectrum as employed in previous work) of two samples of stibnite which had not been subjected to heat treatment. They are in agreement with previous data<sup>5</sup> showing a maximum in the region of  $0.77\mu$ .

Curve 3 *A* depicts the observations obtained on the front side and curve 3 *B* those on the rear side of the fused, then recrystallized, sample. The maximum is at  $0.78\mu$ . From this it appears that aside from a possible slight shift of the maximum to the long wave lengths, the spectrophoto-electrical sensitivity curve of the slowly recrystallized material is not markedly different from the average curve of the original mineral before recrystallization.

#### IV. EFFECT OF ELECTRICAL TREATMENT UPON THE PHOTO-ELECTRICAL SENSITIVITY OF MOLYBDENITE AND STIBNITE.

It is claimed by some experimenters<sup>6</sup> that the photosensitivity of selenium is increased by passing an alternating current through the crystalline material. It was therefore of interest to determine whether the passing of alternating current affects the photo-electrical sensitivity of molybdenite and stibnite.

In this test the crystal was mounted in its usual position for making the photosensitivity tests. By means of additional connections and switches an alternating current from a 2,000-volt transformer could be passed through the crystal for a given period, and immediately thereafter the photosensitivity could be determined without disturbing the crystal.

<sup>4</sup> Coblenz and Kahler, B. S. Sci. Papers, 15, p. 231; 1919.

<sup>5</sup> Coblenz, B. S. Sci. Papers, 16, p. 600; 1920.

<sup>6</sup> In a book by Thomas W. Benson on "Selenium cells—how made" the Fritts selenium cell is described, and mention is made that Fritts increased the sensitivity by passing alternating current through the cell.



It was found that if the alternating current was too large the temperature of the molybdenite was raised by a sufficient amount to cause a temporary decrease in the photosensitivity, which returned to normal if the sample was allowed to cool to room temperature.

Three samples of molybdenite were subjected to alternating-current treatment. Samples were selected which had a low intrinsic photo-electrical sensitivity (ratio of light current : dark current) and also a fairly high sensitivity

#### 1. MOLYBDENITE.

Sample No. 1 of molybdenite was subjected to a small alternating current for 6 minutes, after which the photosensitivity appeared to be increased by perhaps 10 per cent. It was then subjected to 10 additional intervals of electrical treatment varying from 10 to 40 minutes. In the meantime no marked change was observed in the photosensitivity. After standing overnight the intrinsic photosensitivity was found unchanged—at 43 per cent.

Sample No. 2 of molybdenite was subjected to 5 intervals of electrical treatment varying from 10 to 30 minutes each, with resting intervals of 5 minutes to 3 hours, in order to allow the sample to cool. The photosensitivity before treatment was 166 per cent. During the treatment it varied from 67 to 117 per cent. This appeared to be a permanent decrease owing to overheating. It was observed that, in agreement with the results obtained on the direct-heat treatment just described, the specific (dark) resistance appeared to be permanently lowered.

Sample No. 3 of molybdenite was tested because of its low photosensitivity, which was 8.3 per cent before electrical treatment. After a series of alternating-current treatments as above described no change in the sensitivity was observed. Allowing it to rest till the following day, the photosensitivity was found to be 9.2 per cent, which indicates that, within the limits of the experimental errors, no change in photo-electrical sensitivity was produced by passing alternating current through the crystal.

#### 2. STIBNITE.

Sample No. 1 of stibnite,  $\text{Sb}_2\text{S}_3$ , was subjected to four intervals of electrical treatment varying from 5 minutes to 1 hour, with resting intervals of 1 to 2 hours, after which there was found no marked change in the photosensitivity. After resting overnight

the ratio of light current to the dark current was found to be 358 per cent as compared with 348 per cent (difference of only 3 per cent) before treatment.

Similar tests were made on two other samples of stibnite, but no change in photo-electrical sensitivity, either temporary (other than that caused by change in temperature) or permanent could be observed as a result of passing alternating current through the crystal.

The conclusion to be drawn from these experiments is that passing alternating current through the material has no permanent effect upon the photo-electrical sensitivity of molybdenite and stibnite.

## V. ARTIFICIAL PREPARATIONS.

There are several known sulphur compounds of molybdenum,  $\text{MoS}_2$ ,  $\text{MoS}_3$ ,  $\text{MoS}_4$ ; and since the photo-electrical sensitivity of molybdenite,  $\text{MoS}_2$  is usually localized in small spots, it was deemed of importance to determine whether any of the other sulphides of molybdenum cause these photosensitive spots. Accordingly, a study was made of the photosensitivity of artificially prepared sulphides of molybdenum and of various other metals.

### 1. DRY PROCESS PREPARATION OF $\text{MoS}_2$ .

Under this caption are given the results of tests of photo-electrical sensitivity made upon six samples of  $\text{MoS}_2$  prepared in 1919 and 1920 by Dr. Herbert Kahler at Cornell University, by methods described by Guichard,<sup>7</sup> who thought he had produced "crystalline" and "amorphous"  $\text{MoS}_2$ . The crystalline material is produced by mixing ammonium molybdate, potassium carbonate, and sulphur in proper proportions and heating the same to a high temperature in a porcelain crucible. The so-called amorphous material is formed at a lower temperature than the crystalline by heating ammonium molybdate and sulphur. In some samples of the amorphous  $\text{MoS}_2$  the excess sulphur was removed with  $\text{CS}_2$ . When tested by means of X rays, Dr. Kahler found that the so-called amorphous material is microcrystalline.

#### (a) METHODS OF MOUNTING AND TESTING.

Samples of  $\text{MoS}_2$  which were in the form of a fine powder were packed into flat glass tubes, 20 by 3 by 1 mm, into the ends of

<sup>7</sup> Guichard, *Ann. de Chimie et de Phys.*, (7), 23, p. 498; 1901.



which were inserted fine (No. 32) copper wire terminals securely attached with tin-foil and Wood's alloy.

A second method of mounting consisted in pressing the material into a thin tablet about 10 mm in diameter and 0.1 to 0.3 mm in thickness. For this purpose a container was used consisting of a heavy block (5 by 4 by 4 cm) having a boring 1 cm in diameter, into which heavy bolts could be screwed. The powdered material between mica plates was placed in this boring and pressure applied by means of the compression screws. After pressing the powder into a coherent mass the resulting tablet was cut into strips about 3 mm wide, to the ends of which electrodes of pure tin (0.02 mm in thickness) were attached by means of Wood's alloy.

(b) RESULTS.

All samples of  $\text{MoS}_2$ , whether crystalline or the so-called amorphous material (also the latter when freed from sulphur), were

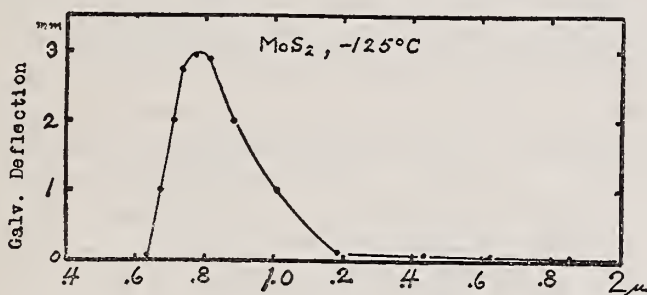


FIG. 2.—Spectrophoto-electrical sensitivity of an artificial preparation of molybdenum sulphide.

found to be photo-electrically sensitive. But the intrinsic sensitivity is very low in comparison with some of the most sensitive samples of the native mineral.

The photo-electrical efficiency (30 to 40 per cent) was practically the same for (1) the samples pressed into flat glass tubes, (2) for the tablets made under high pressure at 20° C., and (3) for these tablets after being held under high pressure and heated to 350° C. for 3 hours. All the samples which do not contain free sulphur have a comparatively low specific resistance.

In Figure 2 is shown the spectrophoto-electrical sensitivity curve of Dr. Kahler's laboratory preparation, sample No. 1, which was prepared in a porcelain crucible at a high temperature, as described on a preceding page.

Owing to its low photo-electrical sensitivity the observations were made at  $-125^{\circ}$  C. The spectrophoto-electrical reaction

curve (for an equal energy spectrum) with a maximum at  $0.8\mu$  resembles that of samples of the native mineral which have a low specific resistance and low photo-electrical sensitivity.<sup>8</sup> In this connection it is relevant to recall that most of the native molybdenite is of relatively low specific resistance and of low photo-electrical sensitivity.

## 2. WET PROCESS PREPARATION OF $\text{MoS}_3$ AND $\text{MoS}_2$ .

The  $\text{MoS}_3$ , also  $\text{MoS}_3 \cdot \text{H}_2\text{O}$ , was obtained by precipitation from a saturated solution of ammonium molybdate with  $\text{H}_2\text{S}$ . This material was a fine powder which was prepared by Mr. F. H. Tucker under the direction of Dr. G. E. F. Lundell of the chemistry division of the Bureau of Standards. Hydrated samples of  $\text{MoS}_3$  were also examined.

### (a) RESULTS.

Tests of several preparations of  $\text{MoS}_3$ , pressed into glass tubes or into tablets as already described, were found to have a high specific resistance and were photo-electrically insensitive.

A sample of  $\text{MoS}_4$ , obtained by precipitation, and probably containing  $\text{MoS}_2$  and  $\text{MoS}_3$ , was found photo-electrically insensitive.

Several samples of  $\text{MoS}_2$  obtained from  $\text{MoS}_3$  by heating in H or  $\text{H}_2\text{S}$  proved to be sensitive, the photo-electrical efficiency of the various samples ranging from 35 to 90 per cent. From this it appears that the photo-electrical sensitivity is inherent in the  $\text{MoS}_2$  and is not the result of the presence of  $\text{MoS}_3$ . This is an interesting result.

## 3. EXPERIMENTS ON MIXTURES WITH $\text{MoS}_2$ .

Small amounts (10 per cent) of metal (Bi, Mo, Se), also of bismuthinite ( $\text{Bi}_2\text{S}_3$ ), of proustite ( $\text{Ag}_3\text{AsS}_3$ ), of cylindrite, of phosphorescent calcium sulphide ( $\text{CaS}_2$ ), of  $\text{UO}_2$ , of  $\text{Th}_2\text{S}_3$ , etc., were mixed with Dr. Kahler's artificially prepared samples of  $\text{MoS}_2$ , either with or without free sulphur, and heated to various temperatures ( $200^\circ\text{C}$ .—for Se, to  $400^\circ\text{C}$ .—for 2 to 3 hours) in the above-mentioned high-pressure container. The results obtained indicated that the photo-electrical efficiency (25 to 40 per cent) is of the same order as that of pure molybdenite.

This information is of interest in showing that the presence of foreign matter did not affect the photosensitivity of  $\text{MoS}_2$ , although it had some effect upon the specific resistance.

<sup>8</sup> Coblenz and Kahler, *B. S. Sci. Papers*, 15, p. 121, (Fig. 27); 1919.

## 4. MISCELLANEOUS PREPARATIONS.

Under this caption a description is given of the preparation and the results of the search for photo-electrical reactions of various substances.

The material was usually in the form of a powder which was pressed into the thin flat glass tubes already mentioned. These tubes were exposed to the total radiation of a standard tungsten lamp, as already described, and the increase in the galvanometer deflection with time observed. This is the reaction-time curve, and in a true photo-electrical response this resistance change is practically instantaneous. This is shown in the first part of curve C, Figure 3, which represents the photo-electrical response of argentite.<sup>9</sup> The dotted part of this curve represents the recovery after exposure.

**MOLYBDENUM OXIDE.**—A photosensitive sample of  $\text{MoS}_2$  was heated to  $640^\circ\text{C}$ . in an electric furnace. The resultant oxide was a coherent pliable lamina (10 by 3 by 0.05 mm) resembling dehydrated mica. The ends were pressed between V-shaped electrodes of pure tin (thickness 0.02 mm) and the oxide tested for photosensitivity.

It was found that, while the oxide is electrically conductive in the dark, it is not photosensitive.

**TIN SULPHIDE,  $\text{SnS}_2 \cdot \text{H}_2\text{O}$ .**—A number of samples of tin sulphide prepared by Dr. Lundell, who had subjected them to different drying treatments including aging for two months, were pressed into the above-mentioned glass tubes and tested for photo-electrical sensitivity. The photo-electrical reaction-time curve A, Figure 3, is practically identical with the rise in temperature, curve B, as indicated on a mercurial thermometer which was similarly exposed to the source of radiation.

Practically identical reaction-time curves were obtained (1) on exposure of the  $\text{SnS}_2$  directly to the lamp and (2) on covering the sample with a thin blackened cardboard box and heating it by the radiations from the lamp which warmed the box.

From this it appears that the observed decrease in electrical resistance is attributable to a rise in temperature of, and not to a true photo-electrical reaction within, the material.

**SULPHIDES OF TUNGSTEN,  $\text{WS}_2$  and  $\text{WS}_3$ .**—The  $\text{WS}_2$  was prepared by Mr. Tucker by fusion of  $\text{WO}_3$  with  $\text{K}_2\text{CO}_3 + \text{S}$ , and precipitated with  $\text{HCl}$ .

<sup>9</sup> Coblentz, B. S. Sci. Papers, No. 446; 1922.



In Figure 4 curve *A* depicts the decrease in electrical resistance when the material was exposed directly to the lamp, and curve *B* shows the decrease when the sample was heated under a thin blackened cardboard box which was exposed to the lamp. For curve *B*, the reaction on exposure and the lag in the recovery after exposure is exactly what one would expect to obtain when there is no true photo-electrical reaction and the decrease in resistance is caused by a temperature rise of the material.

Similar results were obtained for  $WS_2$ , showing no true photo-electrical action.

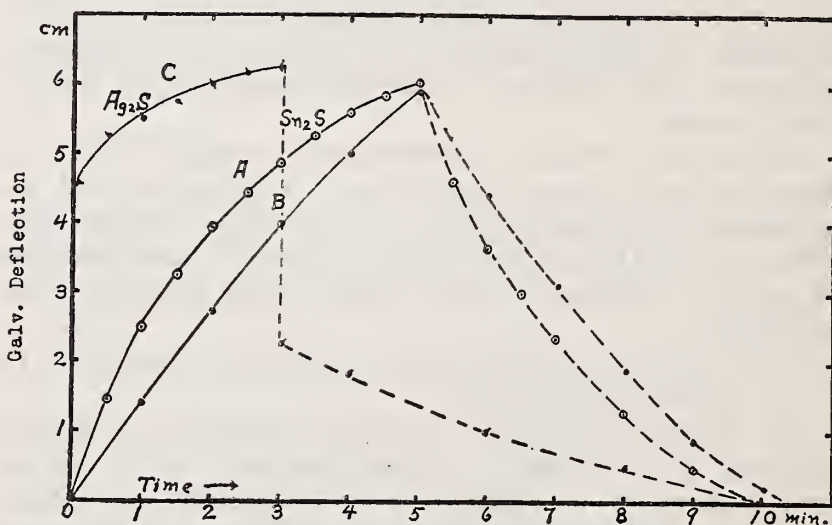


FIG. 3.—Photo-electrical reaction-time curves (*A* and *C*) and temperature rise of thermometer (curve *B*).

URANYL SULPHIDE,  $UO_2S$ .—This material was a brown powder prepared by Mr. Tucker by precipitation from uranium acetate by ammonium sulphide. One sample was heated in a current of  $H_2S$ , forming a black powder. Judged by the reaction-time curves, which are similar to those given in Figure 4, this sulphide showed no marked photo-electrical sensitivity.

$MoSe_3$ .—This selenide was made by precipitation from  $(NH_4)_2MoO_4$  with  $H_2Se$ . This material showed no marked photo-electrical sensitivity.

$Bi_2Te_3$ .—Made by fusion of Bi and Te. This material did not exhibit photo-electrical sensitivity.

$AgNO_3$  and  $KNO_3$ .—These two salts were examined in connection with an investigation of the photo-electrical sensitivity

of the halide salts of silver (B. S. Sci. Papers, No. 456). They did not exhibit photo-electrical sensitivity throughout the spectrum extending from  $0.3\mu$  to  $2\mu$ .

## VI. SPECTROSCOPIC AND CHEMICAL ANALYSIS OF MOLYBDENITE.

As shown in a previous paper,<sup>10</sup> of the samples of molybdenite examined from 17 different mines, only one had a high photo-electrical sensitivity and a high specific resistance. All the other sources yielded material having a low photo-electrical sensitivity and a low specific resistance.

In view of these facts the logical procedure was to obtain spectroscopic and chemical analyses of these two types of material.

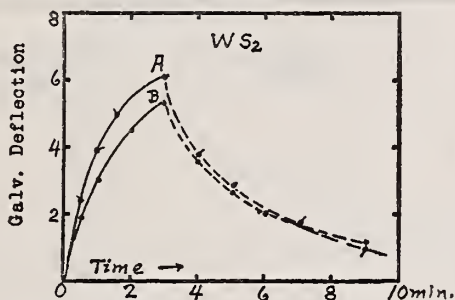


FIG. 4.—Photo-electrical reaction-time curves of  $W S_2$ .

### 1. SPECTROSCOPIC ANALYSIS.

Samples of the photo-electrically sensitive and nonsensitive molybdenite were submitted to Dr. W. F. Meggers of the spectroscopy section for analysis by means of arc spectra.

The spectroscopic analysis showed that the spectra of the metallic elements were identical except that the photosensitive sample contained a trace of magnesium which did not seem to be present in the nonsensitive sample.

In the Bunsen flame the sodium lines appear brighter from heating the sensitive material than the nonsensitive molybdenite.

### 2. CHEMICAL ANALYSIS.

The chemical qualitative analysis was made by Mr. F. H. Tucker, then in the chemical division of this bureau. The results are shown in Table 1. The main difference in these two kinds of molybdenite appears to be the larger iron content in the material of high photo-electrical sensitivity.

<sup>10</sup> Coblentz and Kahler, B. S. Sci. Papers, 15, p. 121; 1919.

TABLE 1.—Chemical Qualitative Analysis of Molybdenite.

[The photosensitive sample No. 1 came from Australia; the nonsensitive sample from Wakefield, Canada.]

Element.	Photosensitive No. 1.	Nonsensitive No. 2.	Element.	Photosensitive No. 1.	Nonsensitive No. 2.
Bi.....	Not found.....	Not found.....	Mn.....	Not found.....	Not found.....
Ca.....	do.....	Do.....	Pb.....	do.....	Do.....
Cu.....	do.....	Do.....	Se.....	do.....	Do.....
Fe.....	Appreciable.....	Trace.....	Sn.....	do.....	Do.....
Mg.....	Trace.....	Do.....	Tl.....	do.....	Do.....

## VII. PHOTOPOSITIVE AND PHOTONEGATIVE REACTIONS IN MOLYBDENITE.

In a previous paper <sup>11</sup> data were given on an unusual sample of molybdenite which, for radiation stimuli of certain wave

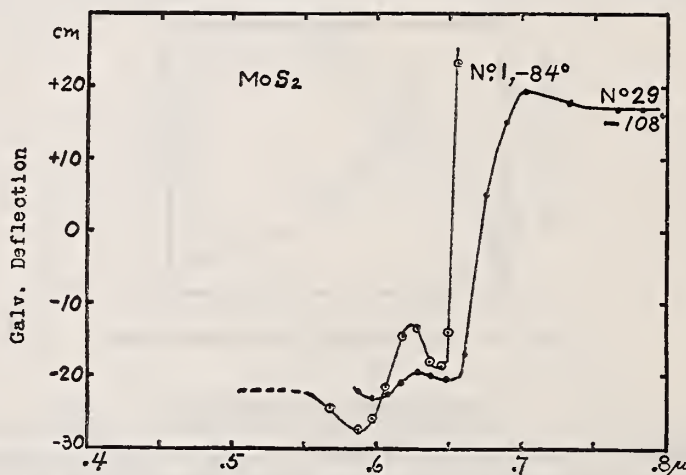


FIG. 5.—Positive and negative spectrophoto-electrical reaction curves of two samples of molybdenite.

lengths but of equal energy, exhibited an increase in resistance instead of the usual decrease in resistance. This phenomenon appears to be rather rare, hence it seemed desirable to search for additional samples exhibiting the photonegative reaction. Ten selected samples of the Australian material which on a preliminary examination showed a strong photo-electrical reaction, were mounted in the usual manner <sup>12</sup> and their spectrophoto-electrical sensitivity tested at low temperatures. Two of these samples exhibited unusual properties which will now be described.

Molybdenite sample No. 29 exhibited a strong negative spectrophoto-electrical reaction at low temperatures. This is illustrated in Figures 5 and 6. In Figure 5 is given also a spectrophoto-

<sup>11</sup> Coblenz, B. S. Sci. Papers, 16, p. 596; 1920.

<sup>12</sup> Coblenz and Kahler, B. S. Sci. Papers, 15, p. 121; 1919.



electrical reaction curve of molybdenite sample No. 1, previously described to show that the general character of the photonegative reaction is the same in the two samples.

### 1. EFFECT OF INTENSITY ON THE PHOTONEGATIVE REACTION.

In Figure 6 is depicted the photo-electrical reaction of sample No. 29 when exposed to spectral radiation intensities  $E = 1$ , 7, and 14. From this it appears that there is an actual decrease in the magnitude of the photonegative reaction on increasing the radiation stimulus from the intensity  $E = 7$  to  $E = 14$ .

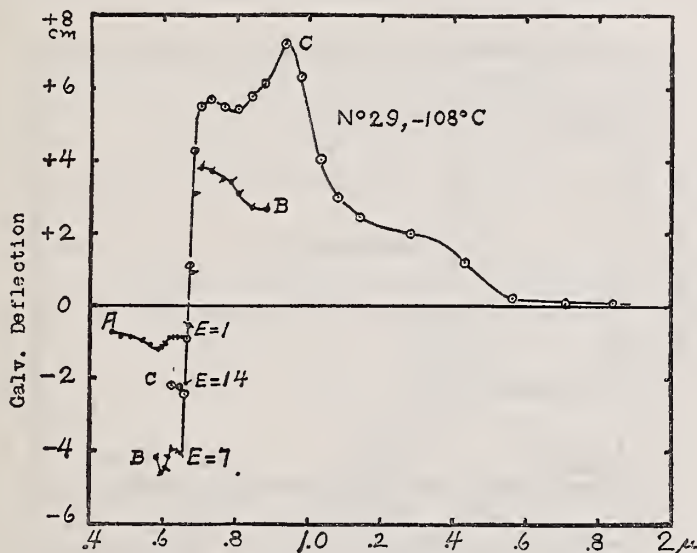


FIG. 6.—Effect of intensity upon the negative photo-electrical reaction in molybdenite sample No. 29.

Since the photonegative reaction is greatly affected by a small change in temperature, a separate test was made of the reaction at  $0.638\mu$  for  $E = 7$  and  $E = 14$ , the temperature being held constant to  $0.02^\circ \text{C}$ . For  $E = 7$ , the galvanometer deflection varied from 41 to 42 mm (for different sets), which agreed well with the observations for curve B, Figure 6. On the other hand, the different sets of observations for  $E = 14$ , which were made alternately with those for  $E = 7$ , were subject to greater fluctuations varying from 24 to 30 mm. The cause of this greater fluctuation, as well as the reduction in magnitude, of the negative spectrophotoelectrical reaction with increase in intensity of the radiation stimulus remains for further investigation. In this connection it is to be noted that the photonegative reaction is confined to a

very small spot in the crystal, and on the higher intensity the effect of the surrounding medium (which is photopositive for all wave lengths of the radiation stimulus) may become perceptible.

## 2. AN EQUAL RESPONSE TO EQUAL ENERGY SPECTRUM.

Experimenters have been searching for a photo-electrical radiometer which reacts proportionately to the intensity of the radiation stimulus and is nonselective to radiations extending over a wide range of the spectrum. Such a radiometer would be useful, though it is not absolutely necessary in a physical photometer.

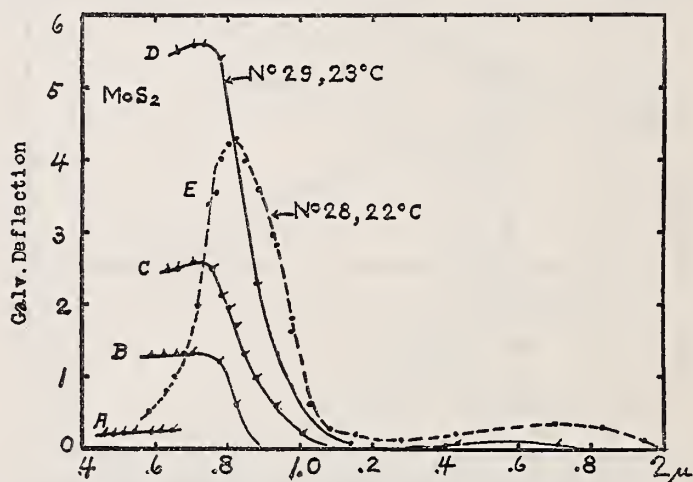


FIG. 7.—Spectrophoto-electrical reaction curves of  $\text{MoS}_2$  samples Nos. 28 and 29 at room temperature.

Molybdenite sample No. 29 is remarkable in having its spectrophoto-electrical reaction at  $23^\circ\text{C}$ . confined practically to the visible and near infra-red spectrum. This is illustrated in Figure 7, curve *D*, which gives the spectrophoto-electrical reaction of the most sensitive part of this sample, which exhibits the photo-negative reaction at low temperatures.

Curves *A*, *B*, and *C* depict the spectrophoto-electrical reactions for an adjacent photo-positive part of the crystal for spectral radiation intensities  $E = 1, 7,$  and  $14$ , respectively. In the visible spectrum the response increases but slightly and uniformly with wave length, and it is proportional to the intensity of the radiation stimulus.

This is the first case observed in which the response is even approximately proportional to the intensity of the radiation stimulus, and is fairly uniform over a wide range of the spectrum.

From this it appears that the time may come when one can prepare samples of molybdenite which will have these properties.

It is, of course, to be understood that for use as a physical photometer, the substance having the above-mentioned photo-electrical properties can be combined with a screen which has a transmission curve coinciding with the visibility curve of the average eye, as now used with a thermopile. The transmissive properties of such a screen would require but little modification for use with molybdenite sample No. 29, as compared with the screen that must be used with the barium photo-electric cell. (See Fig. 8.)

In Figure 7 curve *E* depicts the spectrophoto-electrical sensitivity of molybdenite sample No. 28, and is given to illustrate the less commonly found reaction which is confined practically to a single band at  $0.82\mu$  with a slight reaction at  $1.8\mu$ . This agrees with previous observations on samples Nos. 4 and 10. (B. S. Sci. Papers, No. 338.)

As previously observed on samples Nos. 4 and 10 of molybdenite, having a single maximum at  $0.8\mu$ , the present samples (Nos. 28 and 29) are remarkable for their quickness in attaining photo-electrical equilibrium, the maximum deflection being obtained in 4 to 5 seconds, irrespective of the wave length of the radiation stimulus.

From the data given in the present paper, as well as in previous publications, it appears that molybdenite has a great variety of spectrophoto-electrical reaction curves. The only other substance thus far found which exhibits such a great variety of spectrophoto-electrical reactions is selenium.

#### VIII. PHOTO-ELECTRICAL SENSITIVITY OF MOLYBDENITE AND STIBNITE IN THE ULTRA-VIOLET SPECTRUM.

In connection with observations on silver sulphide and several other substances (Sci. Papers Nos. 446 and 451) exhibiting photo-electrical sensitivity in the ultra-violet, it was of interest to examine also molybdenite and stibnite.

For this purpose the intense lines of the quartz mercury arc were used as radiation stimuli (of equal energy value) as described in previous papers.

Observations were made on  $\text{MoS}_2$ , sample No. 4, which has but a single maximum in the infra-red.<sup>13</sup> Qualitative measure-

<sup>13</sup> B. S. Sci. Papers, 15, p. 121; 1919.



ments from  $0.25\mu$  to  $0.3\mu$  and quantitative measurements from  $0.305\mu$  to  $0.436\mu$  showed that  $\text{MoS}_2$ , sample No. 4 (at  $22^\circ\text{C}$ .), decreases slowly and uniformly in sensitivity with decrease in wave length throughout the ultra-violet.

Similar observations on  $\text{MoS}_2$ , No. 29, described on a previous page, has a uniform photo-electrical sensitivity throughout the ultra-violet.

From these data it appears that sharp bands of photo-electrical sensitivity are absent in the ultra-violet reaction spectrum of molybdenite.

Similar measurements on stibnite, sample No. 1, previously described,<sup>14</sup> showed a gradual decrease in photo-electrical sensitivity with decrease in wave length in the ultra-violet.

From these measurements it appears that molybdenite and stibnite have no sharp bands of photo-electrical sensitivity in the ultra-violet similar to those observed in silver sulphide, cuprous oxide, and the halide salts of thallium.

#### IX. SPECTRAL RESPONSE CURVES OF CASE'S BARIUM AND STRONTIUM PHOTO-ELECTRIC CELLS.

These cells are based upon the discovery<sup>15</sup> of the photo-electrical activity of the deposit which sometimes appears on the plates of high-vacuum audion bulbs having oxide coated filaments.

The cells are highly evacuated, and hence the photo-electrical reaction is free from the phenomena of gasionic conduction. The photo-electric current increases with increase in the applied voltage up to a fixed point—the saturation point. Using voltages which are higher than that required for saturation, the photo-electric current is reported to be proportional to the intensity of the light, and the action is practically instantaneous.

The photoactive material is probably not the pure metal but a mixture with the "suboxide" of the metal.

In Figure 8 curve *A* depicts the spectrophoto-electrical response of a strontium cell (No. 383), with a maximum in the region of  $0.39\mu$ .

Curve *B* gives the spectrophoto-electrical reaction of a barium cell (No. 380). This substance is conspicuous for its high photo-electrical sensitivity throughout the visible spectrum, with a maximum at  $0.42\mu$ .

These two cells are interesting in showing the shifting of the maximum of the spectrophoto-electrical reaction toward the long

<sup>14</sup> B. S. Sci. Papers, 16, p. 600; 1920.

<sup>15</sup> Case, Phys. Rev. (2), 7, p. 398; 1921.

wave lengths with increase in atomic weight, as previously observed in the alkali metals.

Curve C gives the spectrophoto-electrical reaction of cell No. 381, consisting of barium and 5 per cent strontium. The presence of the strontium produces a relatively steeper curve, with a weaker reaction in the red than obtains in the pure barium cell.

In the manufacture of these cells the object in view is the production of a device which can be used as a physical photometer for daylight recording, etc. For this purpose the photo-electric cell is to be covered with a suitable (yellow glass) screen, which reduces the sensitivity in the violet end of the spectrum.

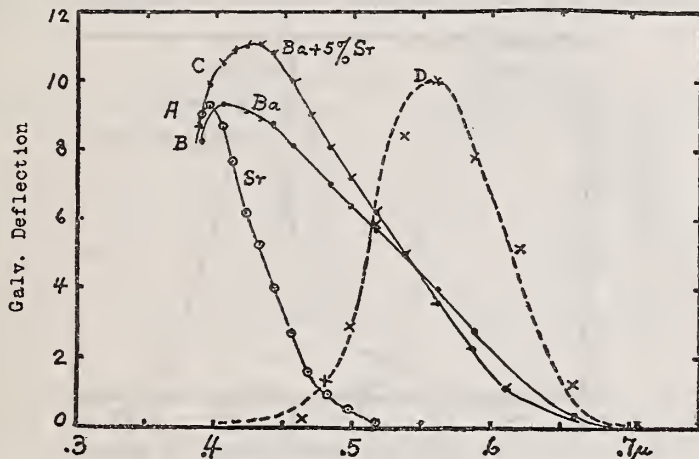


FIG. 8.—Spectrophoto-electrical reaction curves of Case's new Ba and Sr photo-electrical cells.

In Figure 8 the dotted curve, D, is the visibility curve of the average eye. The points marked with the crosses (×××) give the spectrophoto-electrical reaction of barium cell No. 380 when covered with a brownish-yellow screen. The agreement between the photo-electrical response curve and the visibility curve is remarkably close, showing that the production of an exact match is merely a matter of patience in making up a suitable screen.

## X. SPECTROPHOTO-ELECTRICAL SENSITIVITY OF CUPROUS OXIDE AND OF LEAD-ANTIMONY SULPHIDE.

These substances were kindly supplied by the Case Research Laboratory.

### 1. CUPROUS OXIDE.

In Figure 9 is given the spectrophoto-electrical reaction curve of a sample of cuprous oxide,  $\text{Cu}_2\text{O}$ , in the form of a single semi-

translucent red crystal (size about 10 by 5 by 1.5 mm) mounted in an evacuated glass bulb.

The observations were made with a lens spectrometer having a rather wide slit. This probably explains the lack of resolution of the small maximum at  $0.62\mu$ , observed by Pfund.<sup>16</sup> This substance is conspicuous for its high photo-electrical sensitivity in the blue-green of the visible spectrum.

## 2. LEAD-ANTIMONY SULPHIDE.

The source of the sample of lead antimony sulphide,  $Pb_3SbS_3$ , examined is uncertain—probably from lower California. In the letter transmitting the material Mr. Case mentioned that this

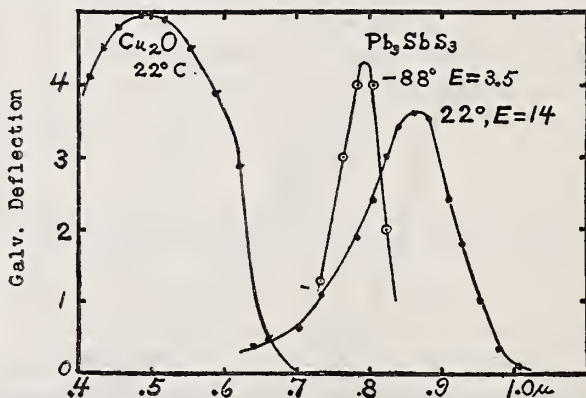


FIG. 9.—Spectrophoto-electrical reaction curves of cuprous oxide and of lead-antimony sulphide.

material differed slightly from the lead-antimony sulphides listed in mineralogy books, being more stable than any of the others.

At room temperature the maximum of the spectrophoto-electrical reaction of  $Pb_3SbS_3$ , observed in the usual manner with a mirror spectrometer and a quartz prism, occurs at  $0.87\mu$ . At  $-88^\circ\text{C}$ . the maximum is shifted to  $0.79\mu$ . These data are interesting in supplementing previous observations<sup>17</sup> showing that the photo-electrical reaction spectrum of a compound is different from that of the constituents. In stibnite,  $Sb_2S_3$ , the maximum occurs at  $0.77\mu$ .

(a) BOULANGERITE AND JAMESONITE.—In a previous paper<sup>18</sup> it was shown that boulangerite,  $Pb_3Sb_3S_6$ , and jamesonite,  $Pb_2Sb_2S_5$ , change in resistance when exposed to light.

<sup>16</sup> Pfund, *Phys. Rev.* (2), 7, p. 289; 1916.

<sup>17</sup> B. S. Sci. Papers, No. 451; 1922.

<sup>18</sup> B. S. Bull., 14, p. 591; 1918.



The spectrophoto-electrical sensitivity of samples of these two minerals was recently tested at room temperature and at low temperatures, but for the spectral intensities available no photo-electrical responses could be obtained.

#### XI. SPECTROPHOTO-ELECTRICAL SENSITIVITY OF IODINE.

In connection with an investigation of the photo-electrical sensitivity of the halide salts of thallium, lead, and silver,<sup>19</sup> an examination was made also of iodine.

For this purpose some freshly crystallized iodine was melted into a uniform layer, about 10 by 5 mm, between thin glass plates. The electrodes were platinum wires 0.1 mm in diameter, separated about 3 mm. The conducting layer of iodine was about 10 by 3 by 0.1 mm. The edges of the glass plates were covered with paraffin to prevent evaporation. By means of the total radiation from a 600-watt gas-filled tungsten lamp, also from a quartz mercury lamp, it was found that iodine reacts to visible radiation. Its photo-electrical sensitivity was found to be so low that no reaction could be observed when exposed to spectral radiation.

By means of a series of screens which transmit regions of the spectrum,<sup>20</sup> it was established that the photo-electrical reaction of iodine lies in the spectral region transmitted by Crooke's sage green (ferrous No. 3) glass,<sup>21</sup> between  $0.4\mu$  and  $0.7\mu$ , with a maximum in the region of  $0.53\mu$  to  $0.55\mu$ . The reasons for believing that the spectrophoto-electrical reaction curve is practically the same as the transmission curve of this glass in the visible spectrum are as follows: (1) Focusing upon the sample the intense line of the quartz mercury arc lamp at  $0.365\mu$ , transmitted by Corning glass 586 J, produced no photo-electrical reaction; (2) on exposure of the iodine sample to the radiation from the gas-filled tungsten lamp, transmitted by Schott's Jena red glasses Nos. 4512 and 2745, it was found that the photo-electrical reaction in the red is small and is confined to the spectral region lying between  $0.6\mu$  and  $0.7\mu$ ; (3) within experimental errors the galvanometer deflection obtained when the iodine was exposed through the sage-green glass (and water cell) after correction for the maximum transmission (45 per cent) of the glass at  $0.53\mu$  was practically the same as that observed when the sample was exposed to the lamp with only the water cell intervening.

<sup>19</sup> B. S. Sci. Papers No. 456.

<sup>20</sup> B. S. Sci. Papers, 15 p. 1341 1919.

<sup>21</sup> The transmission curve of this sample is given in B. S. Tech. Papers No. 93, Figure 2.

It is interesting to note that this maximum does not coincide with that of Tl I at  $0.46\mu$  and Ag I at  $0.5\mu$ . It is hardly permissible to identify the maximum of Pb I<sub>2</sub> at  $0.52\mu$  with the one for pure iodine.

In order to definitely identify the bands of the halogen salts of thallium, lead, and silver with the constituent acid element, an examination must be made of Cl and Br for photo-electrical sensitivity.

## XII. SUMMARY.

The purpose of this paper is to give miscellaneous data which were obtained in connection with the general investigation of photo-electrical sensitivity, but not heretofore published.

Data are given on the preparation and testing of various sulphides of molybdenum, MoS<sub>2</sub>, MoS<sub>3</sub>, etc., the object in view being the artificial production of molybdenite MoS<sub>2</sub>, which is photo-electrically sensitive.

The results thus far obtained show that all the wet and dry process preparations of MoS<sub>2</sub> are photo-electrically sensitive, but the intrinsic sensitivity is far less than that of the photosensitive spots found in some samples of the natural mineral.

From the data at hand it appears that this photo-electrical sensitivity is inherent in the MoS<sub>2</sub>.

Spectroscopic and qualitative chemical analysis shows no marked difference in the constituents of samples of molybdenite, excepting a larger iron content in the material having a high photo-electrical sensitivity.

A number of samples of molybdenite were subjected to heat treatment (1) by passing electrical current through them and (3) by heating them, in some cases under high pressure, in an oven.

The conclusion to be drawn from these tests is that slow heat treatment has no marked permanent effect upon the intrinsic photo-electrical sensitivity in the temperature range up to  $500^{\circ}$  C. At a temperature of about  $600^{\circ}$  C. the sensitivity appears to be permanently decreased. Raising the temperature to a low red (about  $700^{\circ}$  C.) heat destroyed the photosensitivity.

In the heat treatment of stibnite it was found that, aside from a possible shift of the maximum toward the long wave lengths, the spectrophoto-electrical sensitivity curve of the melted and slowly recrystallized material is practically the same as that of the average curve of the native mineral.

Samples of molybdenite and stibnite were subjected to electrical treatment which consisted in passing alternating current through them for certain intervals of time and then noting the effect upon the photo-electrical sensitivity. The conclusion to be drawn from these experiments is that alternating current has no marked permanent effect upon the photo-electrical sensitivity of molybdenite and stibnite.

Among the miscellaneous artificial preparations examined for photo-electrical sensitivity were molybdenum oxide; various sulphides of tin, tungsten, and uranium; also  $\text{Bi}_2\text{Te}_3$ ,  $\text{MoSe}_3$ ,  $\text{AgNO}_3$  and  $\text{KNO}_3$ . None of these preparations showed a marked photo-electrical sensitivity.

Data are given on the negative spectrophoto-electrical reaction in molybdenite, confirming and extending previous observations.

A sample of molybdenite was found which has a uniform sensitivity over a wide range of the visible spectrum, and a photo-electrical reaction which is proportional to the intensity of the radiation stimulus. This lends encouragement to the efforts which should be made to produce, for radiometers, a photo-electrical material which will have these properties.

From a special examination of these two minerals it appears that molybdenite and stibnite have no sharp bands of photo-electrical sensitivity in the extreme ultra-violet, but that the reaction gradually decreases with decrease in wave length.

Several spectral response curves are given of Case's barium and strontium photo-electric cells, which have maxima at  $0.42\mu$  and  $0.39\mu$ , respectively. By covering the barium cell with a suitable screen a spectral response curve is obtained which coincides closely with the visual response of the average eye.

Data are given on the spectrophoto-electrical reaction of cuprous oxide; also of a lead antimony sulphide,  $\text{Pb}_3\text{SbS}_3$ , which shows that the spectrophoto-electrical reaction spectrum of a compound is not the composite of the reactions of the constituents which may be photo-electrically sensitive.

Iodine was found to be photo-electrically sensitive with a maximum in the region of  $0.53\mu$  to  $0.55\mu$ .

WASHINGTON, August 30, 1922.



[The text on this page is extremely faint and illegible. It appears to be a multi-paragraph document, possibly a letter or a report, but the specific content cannot be discerned.]

