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## Thallous Sulfide Photo-Conductive Cells

### I. Experimental Investigation\*

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(Received March 4, 1946)

An experimental study of thallous sulfide photo-conductive cells is presented. It includes an investigation of the sensitizing oxidation reaction; cell characteristics as function of voltage, temperature, light intensity, wave-length, modulating frequency, and composition; measurements of thermoeffect and optical absorption; x-ray and electron diffraction studies, and an examination of the photo-response to light flashes of very short duration. A theoretical discussion will be given as Part II in a subsequent paper.

### INTRODUCTION

THE photo-sensitivity of oxidized thallous sulfide was discovered by T. W. Case in 1917. Since his initial work<sup>1</sup> some progress has been made in improving the stability and response of this photo-conductive cell<sup>2,3</sup> as a result of empirically developed<sup>4-6</sup> and undisclosed<sup>2</sup> processes of manufacture. More recently the photo-cell, as further developed by R. J. Cashman,<sup>7</sup> has become of importance in this country for war communication systems, but its usefulness at present is limited by lack of appreciable sensitivity above a wave-length of  $1.2\mu$  and by

poor frequency response.<sup>8</sup> A fundamental study was therefore undertaken with the objective of gaining insight into the photoelectric mechanism, as such knowledge should be of considerable assistance in understanding and improving the cell properties.

### I. PREPARATION OF THALLOUS SULFIDE

Three batches of thallous sulfide were prepared\* by two different methods. In the first of these, thallous sulfide was precipitated by means of hydrogen sulfide from an ammoniacal solution containing thrice recrystallized thallous sulfate. The deposit was washed, dried, and fused in vacuum, yielding a product of reasonable purity (see analysis of sample No. 1 in Table I). However, owing to unavoidable oxidation in the course of handling the finely divided precipitate under atmospheric conditions, this batch of material was used only for exploratory experiments.

\* This research was carried out under contract OEMsr-1036 with Division 16, Section 16.4, of the National Defense Research Committee and completed in June, 1945. Publication has been delayed because of the war.

\*\* Deceased.

<sup>1</sup> T. W. Case, *Phys. Rev.* **15**, 289 (1920).

<sup>2</sup> R. Sewig, *Zeits. f. tech. Physik* **11**, 269 (1930).

<sup>3</sup> W. Leo and C. Mueller, *Physik. Zeits.* **36**, 113 (1935).

<sup>4</sup> Q. Majorana and G. Tedesco, *Atti accad. Lincei* **8**, 9 (1928).

<sup>5</sup> F. Michelssen, *Zeits. f. tech. Physik* **11**, 511 (1930).

<sup>6</sup> A. A. Sivkov, *J. Tech. Phys. U.S.S.R.* **8**, 11 (1938).

<sup>7</sup> R. J. Cashman, N.D.R.C. Report No. 16.4-6 (1943).

<sup>8</sup> W. L. Hole and R. J. Cashman, N.D.R.C. Report No. 16.4-7 (1943).

\* The preparation of the material was the work of M. C. Bloom and J. P. Levy.

TABLE I. Spectrographic analyses.

Material	Al	Cu	Fe	Ca	Impurities, parts per million		Mg	Ni	Pb	B
					Ag	Na				
Tl <sub>2</sub> S No. 1 (pptn.)	6	4	4	25	—	40	10	5	35	—
Tl <sub>2</sub> S No. 2 (synthesis)	0.5	2	0.5	0.5	<.04	.04	.1	<1	>100	—
Tl <sub>2</sub> S No. 3 (synthesis)	1	8	<1	1	<.05	<1	<.3	<2	3	<2

The other batches were prepared by reacting stoichiometric quantities of thallium and sulfur at elevated temperatures in evacuated quartz apparatus. The sulfur was purified by the method of Bacon and Fanelli.<sup>9</sup> In the case of sample No. 2, C.P. thallium metal, which had been melted and strained in vacuum to remove oxide, was employed. A more elaborate procedure was followed in purifying the metal in the preparation of sample No. 3, consisting of three successive fractional crystallizations of thallous sulfate, cathodic deposition of thallium from the saturated sulfate solution acidified with dilute sulfuric acid, washing, drying, and melting and straining in vacuum. This latter sample was also stirred with nitrogen during the reaction to assure homogeneity throughout the melt.

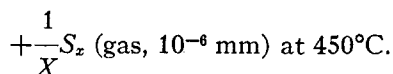
Table I summarizes the spectrographic analyses of the different thallous sulfide products.

Sample No. 2 was employed in the majority of the experiments described in this paper. Sample No. 3, available only in the later stages of the research, served to demonstrate that the photo-sensitivity of thallous sulfide originates from its oxygen content and not from accidental impurities.

## II. THERMAL STABILITY OF THALLOUS SULFIDE

Inasmuch as thallous sulfide is evaporated in vacuum as the first step in preparing photo-cells, its thermal stability is of great importance. From known values of free energy content and heat of formation, calculation\* was made of the change in free energy attending the change in state:

Tl<sub>2</sub>S (solid) → 2 Tl (liquid)



The calculation assumes that  $S_x$  is made up of an

<sup>9</sup> R. F. Bacon and R. Fanelli, Ind. Eng. Chem. **34**, 1043 (1942).

\* Calculation performed by J. H. Schulman.

approximately equal mixture of  $S_6$  and  $S_8$  molecules.  $\Delta F$  is positive in sign and amounts to about 20,000 calories, indicating that thallous sulfide will not spontaneously decompose into its elements under the above mentioned conditions.

An attempt was made to confirm this conclusion by heating a thallous sulfide layer, evaporated in the usual type of cell (see Section IV), for several hours in vacuum to progressively higher temperatures. After each heating period the cell was quenched and measurement made of its conductivity, which certainly should be affected by decomposition. No appreciable change in conductivity resulted until at about 400°C the experiment came to an end because the layer sublimed off the grid electrodes.

## III. OXIDATION REACTION

Thallous sulfide is photo-sensitized by oxidation. A study of the oxidation reaction at 250°C and 350°C by gas absorption, and x-ray and electron diffraction methods was therefore undertaken to identify the reaction products.

### A. Gas Absorption Method

It is a prerequisite of accurate gas absorption measurements that the system be of small volume so as to maximize the change in pressure accompanying the reaction. The essential portion of the apparatus employed is sketched in Fig. 1. Volume  $B$  between the stopcocks  $C$  and  $D$  was calibrated with water before sealing to the vacuum system ( $B \sim 45 \text{ cm}^3$ ). The small volume of the Pirani gauge,\*  $P$ , was estimated from the bore of the tubing employed. The reaction vessel comprising the major portion of volume  $A$  ( $A \sim 45 \text{ cm}^3$ ) was made from Nonex glass tubing of 30 mm o.d.

For each reaction vessel, volume  $A$  was cali-

\* A description of a more rugged model of this gauge, which is capable of measuring pressures up to 15 mm, will be published elsewhere.

brated by filling *A* and *B* to a predetermined pressure, evacuating *B*, reconnecting *A* and *B*, and establishing the resulting pressure. A weighed amount of thallous sulfide ( $14.5 \pm 1$  mg in the usual case, known to  $\pm 0.1$  mg) was then introduced into the reaction vessel, the system evacuated, the vessel outgassed at  $400^\circ\text{C}$  for an hour, and the entire sample evaporated by heating with a Bunsen burner (film thickness about 5000Å). To initiate the reaction, the vessel was heated by an oven to the desired temperature, tap *D* closed, oxygen at known temperature introduced into volume *B* to the desired starting pressure, and tap *D* opened. The progress of the reaction was measured by observing the pressure as a function of time at the constant temperature for a period up to twenty hours. The reaction vessel was then quenched by an air blast and the pressure re-measured at room temperature with the whole system in temperature equilibrium. This completes the data required to calculate the composition of the oxidized layer.

Visual observation of thallous sulfide layers oxidized to varying degrees reveals that the photo-cell material consists of two phases; a grayish-black (photo-sensitive) substance and a bright yellow (insulating) material. With progressing oxidation the quantity of the yellow phase increases; and at a composition approximated by 1 mole  $\text{O}_2$  per mole  $\text{Tl}_2\text{S}$ , the black phase completely disappears.

The existence of these phases, and of only these two phases, was confirmed by the x-ray and electron diffraction studies reported below.

### B. X-Ray Diffraction Study

X-ray powder photographs were taken of a number of photo-sensitive layers carefully removed from the cells in a nitrogen atmosphere and sealed in small glass capillaries. A phase found to be present in all sensitive cells gave rise to a diffraction pattern\* correlating satisfactorily with the structure of  $\text{Tl}_2\text{S}$  proposed by Ketelaar and Gorter.<sup>10</sup> Usually a second (yellow) phase was observed in addition. The diagram in Fig. 2 shows the positions and relative intensities of

diffraction lines from patterns obtained with pure  $\text{Tl}_2\text{S}$ , with a typical photo-cell sample and with the yellow material from a "completely" oxidized layer.

Inasmuch as the photo-sensitive phase possesses the same structure as thallous sulfide, it is probably safe to conclude that the former represents a solid solution of oxygen in  $\text{Tl}_2\text{S}$ . The change in lattice constants with composition usually observed in solid solutions, if present, could not be detected in the present case because the small crystallites in the evaporated layers produced diffuse lines in the high  $\theta$  region and prevented accurate measurements.

The interplanar spacings calculated from the diffraction photograph of the yellow phase indicate a face-centered cubic lattice with a cell edge of 10.77Å. Since this phase has a structure differing from any of the known structures of thallium compounds and since its composition is about 1 mole  $\text{O}_2$ /mole  $\text{Tl}_2\text{S}$ , it may be identified as the compound  $\text{Tl}_2\text{SO}_2$ .<sup>11</sup> This substance proved quite stable; it cannot be decomposed at a reasonably rapid rate by heating in vacuum unless a temperature high enough to sublime the material is employed. The gray condensate resulting consists of a mixture of the  $\text{Tl}_2\text{S}$  and  $\text{Tl}_2\text{SO}_2$  phases.

In passing, it may be noted that no changes in structure were observed on heating thallous sulfide up to  $385^\circ\text{C}$ . From the displacement of the

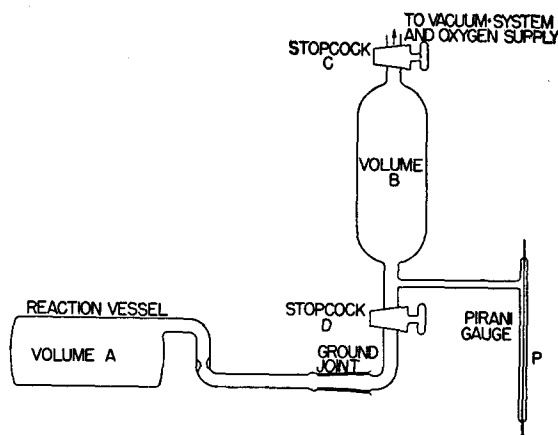


FIG. 1. Reaction vessel, system *A*.

\* This same pattern was obtained with our fused samples of thallous sulfide and with unoxidized evaporated layers.

<sup>10</sup> J. A. A. Ketelaar and E. W. Gorter, *Zeits. f. Krist.* **101**, 367 (1939).

<sup>11</sup> Reference to the existence of this compound has been made by I. I. Iskoldsky, *Mineralnoje Syrye* No. 4, 404 (1931).

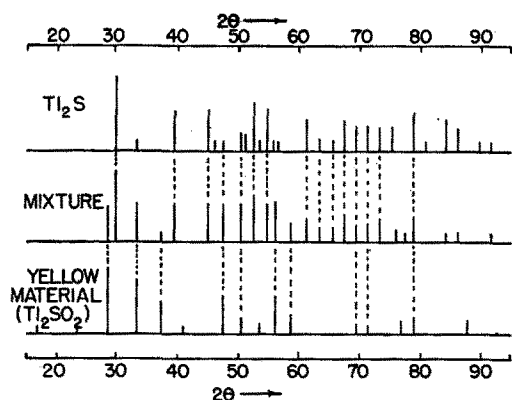


FIG. 2. X-ray diffraction patterns.

(0006) reflection in the x-ray diffraction patterns it was possible to determine the linear coefficient of thermal expansion in the direction of the "c" axis. The value,  $\alpha = 34 \times 10^{-6}$  (20–385°C), does not differ appreciably from that of thallium metal,  $\alpha = 30.3 \times 10^{-6}$ .

### C. Electron Diffraction Study

For the electron diffraction investigation a cell was produced in the diffraction apparatus itself for a study at grazing incidence. On account of the relatively low conductivity of the thallos sulfide, the diffraction specimen charged up if not prepared on a conducting surface. The sample prepared on a glass slide consisted of two parts: a section on aquadag from which the diffraction studies were made and immediately adjacent to it a photo-cell section with its standard gridwork (see Section IV). Thallos sulfide was vacuum evaporated from a small crucible onto the surface of this slide and also onto Formvar Films of thickness about 100Å for transmission studies. Examination of the diffraction patterns obtained (see Fig. 3, *a*+*b*-transmission patterns, *c*-reflection pattern) show the crystals of thallium sulfide to be arranged with their "c" axis preferably oriented in a direction perpendicular to the receiving surface. The slide was then heated for twenty minutes at 250°C at an oxygen pressure of 2 mm, resulting in the development of an appreciable photo-sensitivity. The electron diffraction pattern from the sensitive surface is shown in Fig. 4a; the interplanar spacings check those from the unoxidized  $\text{Ti}_2\text{S}$  pattern. In addition, it may be noted that the original orientation

persists and that the crystallites have grown in size. However, the pattern is considerably more diffuse than that from the unoxidized surface and indicates that the structure has probably been disrupted by solid solution of some oxygen. More complete oxidation produced the pattern shown in Fig. 4b; the interplanar spacings check the x-ray data from the yellow material. Hence, the electron diffraction data lead to the same conclusions as those suggested by the x-ray diffraction results.

## IV. PREPARATION OF CELLS

Cells prepared by a single oxidation treatment at 250° and 350°C were investigated with the purpose of obtaining data on dark resistance and photo-sensitivity as a function of oxygen content. In addition, the reproducibility of the characteristics of photo-cells prepared under closely identical conditions was studied.

### A. Methods

Two vacuum systems of different design were employed in the preparation of these cells. The first one, system *A*, has already been described in Section III A and was used with the following changes. The reaction vessel was furnished with sealed-in tungsten electrodes and an aquadag gridwork as shown in Fig. 5.\* The gridwork covered an effective area of 1"×1" with 16 lines per inch. Pretreatment of the cell blank consisted of a heat treatment in air for several minutes at 400°C followed by a heating in a vacuum for one hour at 500°C. The introduction of sample, outgassing, evaporation, and oxidation were carried out by a procedure similar to that outlined in Section III A. After quenching, the resistance and photo-sensitivity of the cell were determined; the oxygen was pumped out, which did not affect the sensitivity; and the cell was sealed off. Since its properties changed rapidly with time for a few days, the resistance and sensitivity increasing in general, final measurements were postponed until the characteristics had stabilized.

The essential features of the second system, system *B*, which was designed to operate with a large volume (2 liters) of oxygen at pressures of the order of those employed in the commercial

\* After a design of R. J. Cashman.

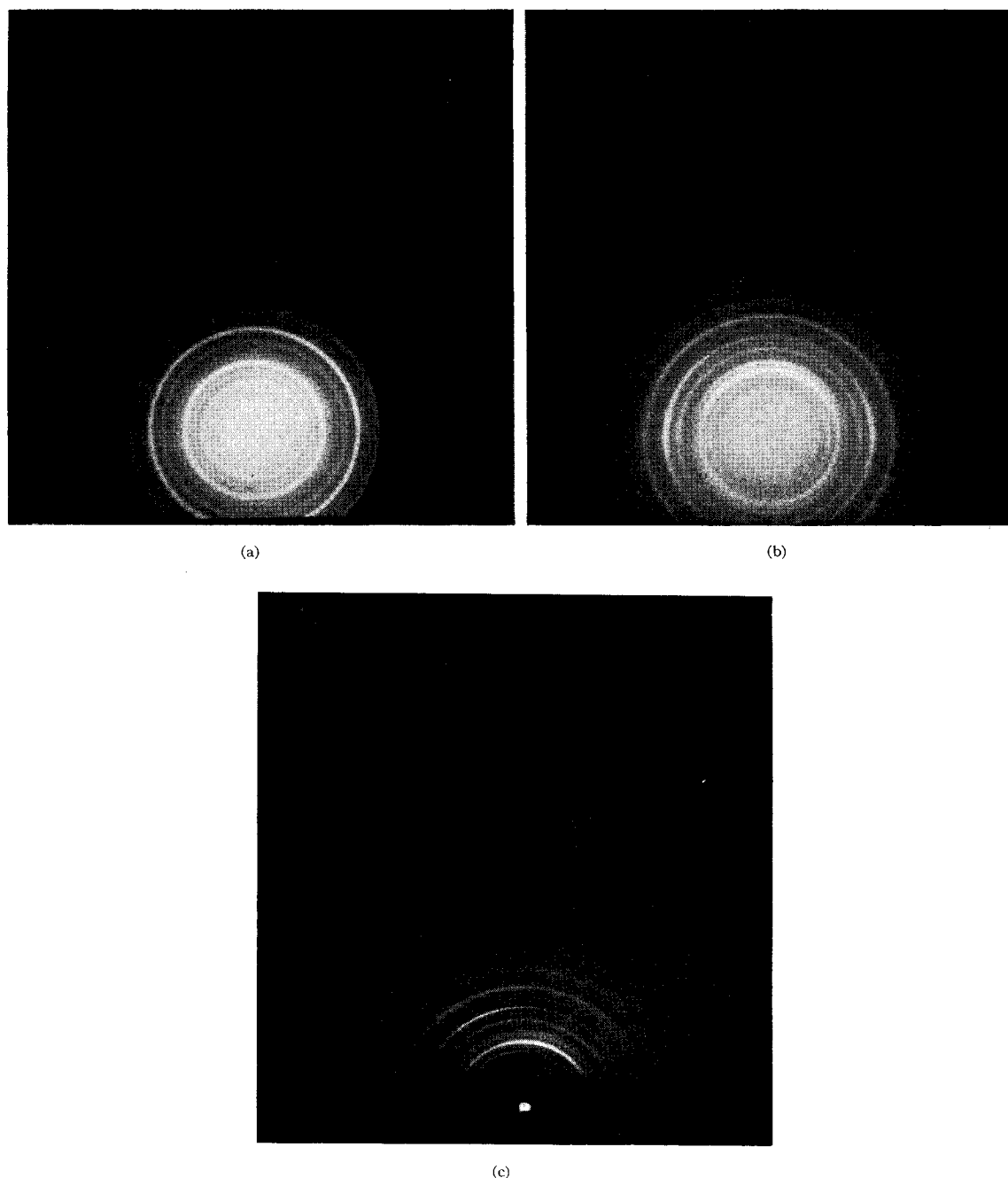


FIG. 3. Electron diffraction patterns of thallous sulfide:  
 (a) electron beam  $\perp$  to  $\text{Tl}_2\text{S}$  film  
 (b)  $\text{Tl}_2\text{S}$  film inclined  $45^\circ$  to electron beam  
 (c) electron beam at grazing incidence to  $\text{Tl}_2\text{S}$  surface.

process,<sup>12</sup> are shown in Fig. 6. The preparation of cells was carried through as before with the minor

<sup>12</sup> C. W. Hewlett, J. J. FitzPatrick, H. T. Wrobel, N.D.R.C. Report 16.4-39 (1945).

exceptions that the volume of the cell blank, *ca.* 40 cc, was not accurately determined, that oxygen was introduced prior to heating, and that the reaction was initiated by covering the cell

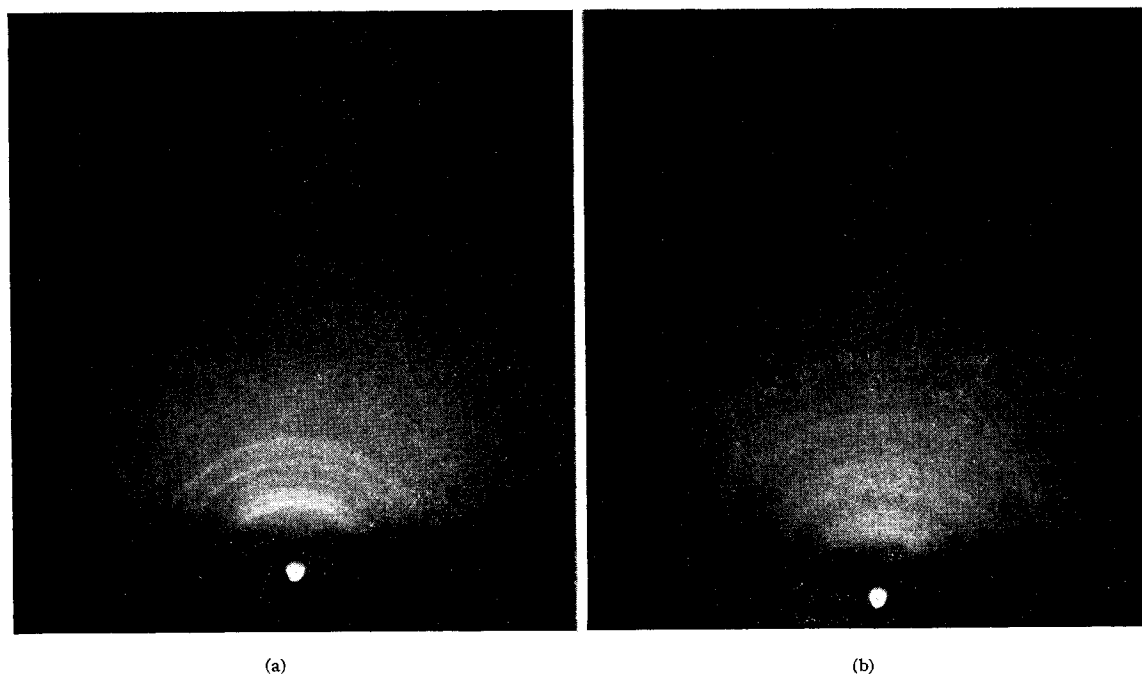


FIG. 4. Electron diffraction patterns of oxidized thallous sulfide layers: (a)  $\text{Tl}_2\text{S}$  phase, (b)  $\text{Tl}_2\text{SO}_2$  phase.

with the hot oven. The oxidation was allowed to proceed for about twenty hours; at the end of this period the cell was quenched, sealed, and measured as described above. The residual pressure was also determined to permit an estimation of oxygen content.\*

### B. Resistance and Photo-Sensitivity as Function of Oxidation

Data on dark resistance, thermal activation energy,  $U$ , and photo-sensitivity of cells, pre-

pared from sample No. 2 in systems *A* and *B* by oxidation at  $250^\circ\text{C}$ , as a function of the composition of the oxidized layer are tabulated in Table II and similar data at  $350^\circ\text{C}$  for system *B* are shown in Table III.\*\*

For the cells prepared at  $250^\circ\text{C}$  there is no discernable relation between thermal activation energy (see Eq. (4)) and oxygen content; however, the dark resistance increases with oxidation until quite sensitive cells are obtained. Beyond this point correlation between resistance and composition is obviated by the large fluctuations in the value of the dark resistance of cells prepared by the same procedure.

Table II shows, in addition, that the minimum amount of oxygen required for producing a sensitive cell varies with the range of pressures employed. Although under the conditions of system *A* about 0.3 mole  $\text{O}_2$ /mole  $\text{Tl}_2\text{S}$  is required, in system *B* about 0.1 mole  $\text{O}_2$ /mole  $\text{Tl}_2\text{S}$  suffices. This apparently results from the simultaneous or successive occurrence of two oxidation products, the relative amounts of which vary in accordance with operating conditions. The absorption of still more oxygen does not improve

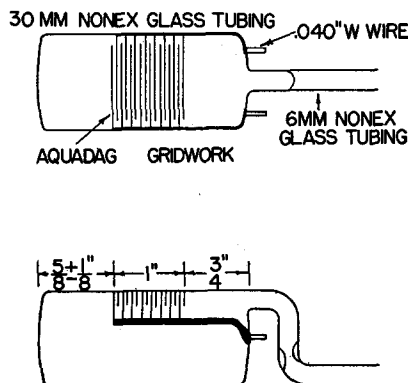


FIG. 5. Cell blank.

\* We are indebted to R. B. Speed for the preparation of cells in system *B*.

\*\* See Section V for details on measurements, definitions of terms, and references.

the photo-conductivity further but converts more of the thallos sulfide phase into  $\text{Ti}_2\text{SO}_2$ . Highly sensitive cells can therefore be made at  $250^\circ\text{C}$  even though the operating pressure varies over wide limits. The variations in sensitivity of cells prepared by the same process are appreciable but not as extreme as the fluctuations in the resistance.

In the case of the cells prepared at  $350^\circ\text{C}$ , the compositions are higher in oxygen than the corresponding ones attained at  $250^\circ\text{C}$  owing to the increased rate of reaction at the higher temperature. The electrical characteristics do not differ fundamentally, however, in the two sets of cells.

#### V. CHARACTERISTICS OF THALLOUS SULFIDE PHOTO-CONDUCTIVE CELLS

A determination of whether the photo-sensitivity of the cell represents a primary or secondary photo-effect is of paramount importance. The sluggishness of the cell,<sup>1,13,14</sup> its strong temperature dependence<sup>1,13</sup> and poor frequency response<sup>2</sup> indicate a secondary type. In addition, Runge and Sewig<sup>15</sup> have concluded from their

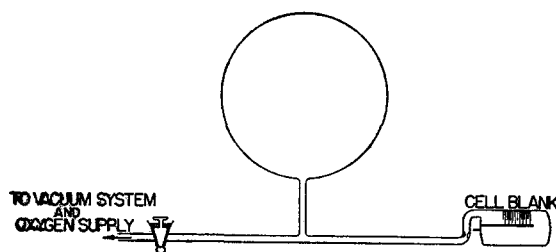


FIG. 6. Reaction vessel, system B.

measurements that light creates disturbance centers which decay exponentially with time. An unequivocal decision can be obtained by a determination of the quantum yield. While a primary photo-effect makes use only of the charge carriers liberated by the absorption of light quanta and is normally limited to a maximum yield of one electron per quantum absorbed, a secondary photo-effect changes the conductivity of the material and quantum yields far exceeding unity may result.

The characteristics of representative Cashman cells\* were investigated as a function of voltage, temperature, light intensity, and wave-length.

TABLE II. Resistance and photo-sensitivity vs. oxidation,  $250^\circ\text{C}$ .

System	Cell No.	Composition, mole $\text{O}_2$ /mole $\text{Ti}_2\text{S}$	Initial pressure, mm	Dark resistance, megohms	Thermal activation energy, electron volts	White light sensitivity Response to 90-cycle modulated light, signal: noise with infrared transmitting filter, <sup>a</sup> db $\Delta I/I_0$ at .023 hololumens per in. <sup>2</sup>
A	2-7	0 <sup>b</sup>	—	.0075-.022	.59 <sup>a</sup>	0
	5	0.119	1.50	.011	.48	.01
	4	0.251	2.92	6.1	.62	2.6
	6	0.339	4.99	28	.47	22
	2	0.578	6.56	225	.61	30
	7	0.760	8.48	45	.46	19
	3	1 <sup>d</sup>	12.65	$\infty$	—	0
B	— <sup>b</sup>	0	—	.022-.11	.54 <sup>a</sup>	0
	72	.06	.025	.055	.52	0.25
	68	.13	.051	187	.79	55
	56, 58, 60,					
	64, 66, 86	.16	.09	1.7-204	.77 <sup>e</sup>	19-198
	24, 40, 50,					
	52, 54, 84	.39	.62	2.5-55	.70 <sup>f</sup>	18-44
	70	.49	1.92	37	.41	35

<sup>a</sup> Without filter S/N ratios are about 12 db higher.

<sup>b</sup> After initial evaporation.

<sup>c</sup> Owing to the high conductivity of the unoxidized material, the resistance of the gridwork is not negligible compared to that of a layer of standard thickness; hence, a much thinner layer was employed.

<sup>d</sup> Sample completely yellow.

<sup>e</sup> Cell No. 64.

<sup>f</sup> Cell No. 54.

<sup>13</sup> W. W. Coblenz, Bur. Stand. J. Research **16**, 254 (1920).

<sup>14</sup> I. Kaplan, J. Opt. Soc. Am. **14**, 253 (1927).

<sup>15</sup> I. Runge and R. Sewig, Zeits. f. Physik **62**, 726 (1930).

\* The gridwork covered an effective area of  $\frac{3}{4}'' \times \frac{1}{4}''$  with a spacing of  $1/30''$  between adjacent lines.



TABLE III. Resistance and photo-sensitivity vs. oxidation, 350°C.

Sample	Cell No.	Composition, mole O <sub>2</sub> /mole TiS	Initial pressure, mm	Dark resistance, megohms	$\Delta I/I_0$ at .023 hololumens/in. <sup>2</sup>	White light sensitivity Response to 90-cycle modulated light, signal: noise with infra-red transmitting filter, db
9C*	138	0.21	0.10	72.5	5.6	48
9C	168	0.30	0.18	10.5	1.7	54
9C	166	0.36	0.18	140	25.8	46
9C	136	0.38	0.16	1.05	33.5	50
2	116	0.16	0.066	0.15	6.8	51
2	114	0.69	0.53	840	25.8	48

\* Material employed in the commercial process.

### A. Apparatus

Monochromatic\*\* radiation was obtained by the use of a Gaertner instrument (L234-HT) with quartz optics, the output of which was focused by a mirror system alternately on the test cell or on a thermocouple.

For determining its temperature dependence, the cell was mounted in an electrically heated housing or in a double-walled container thermostated by circulating liquids.

Three tungsten lamps, covering a wide range of light intensities and calibrated in terms of microwatts as well as microhololumens\*\*\* were employed in "white light" measurements. Tests with square-wave modulated light of one microhololumen peak (without filter) were carried

out on the standard instrument developed at the University of Michigan.<sup>16,17</sup>

### B. Effect of Applied Voltage

For a thallos sulfide cell the dark current,  $I_0$ , and the current,  $I$ , obtained under illumination are proportional to the voltage applied,  $V$ , at constant temperature (Fig. 7); that is

$$I_0 = VG_0 = V/R_0, \quad (1)$$

$$I = I_0 + \Delta I = VG$$

$$= V(G_0 + \Delta G) = \frac{V}{R} = \frac{V}{R_0 - \Delta R}, \quad (2)$$

where  $R_0$  is the dark resistance,  $R$  the resistance under illumination, and  $G_0$  and  $G$  the corresponding conductances.

It follows from Eqs. (1) and (2) that the cell

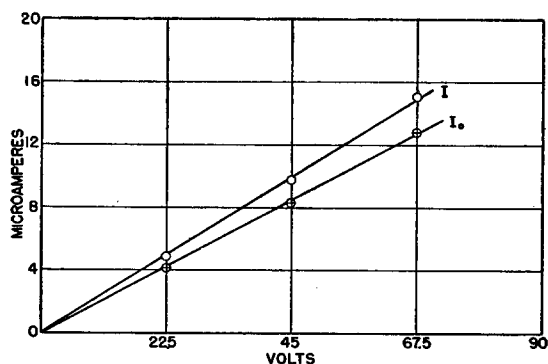


FIG. 7. Dark current,  $I_0$  and total current,  $I$ , obtained with illumination as function of applied voltage ( $\lambda = 0.8\mu$ ;  $F = 0.5$  microwatts).

\*\*  $\Delta\lambda \sim 150\text{\AA}$ .

\*\*\* One hololumen is that radiant flux of all wavelengths which has the spectral distribution characteristic of a tungsten lamp at color temperature 2848°K, and which, evaluated as visible light, equals one lumen. (See N.D.R.C. Report No. 16.4-10 (1943) by G. A. Van Lear, Jr.)

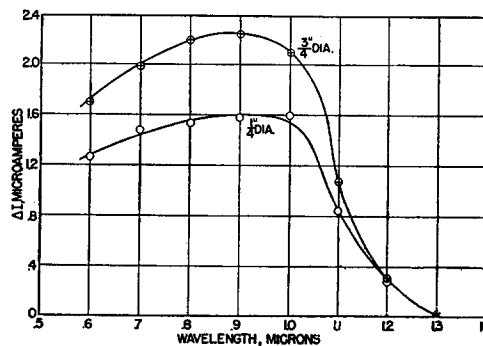


FIG. 8. Effect of spot size on photo-current for constant light input. ( $R_0 = 5.4$  meg.;  $V = 22.5$  v;  $F = 1$  microwatt.)

<sup>16</sup> W. L. Hole, N.D.R.C. Report No. 16.4—Special No. 9 (1944).

<sup>17</sup> L. N. Holland, N.D.R.C. Report No. 16.4—Special No. 6 (1944).

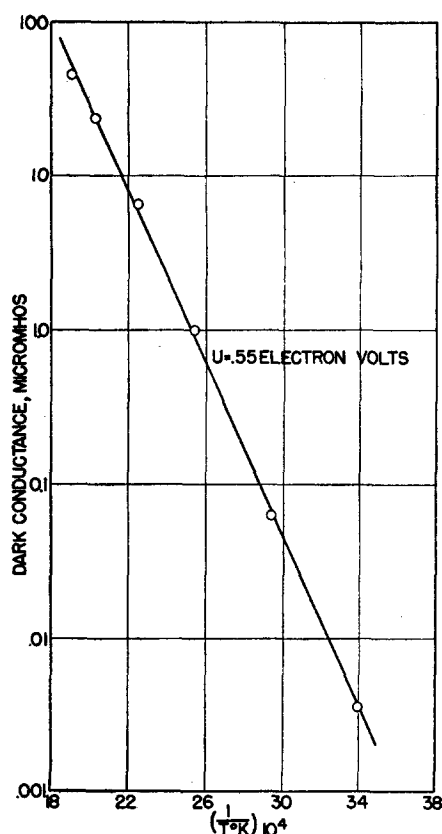


FIG. 9. Temperature dependence of the dark conductance.

sensitivity can be characterized independently of  $V$  by the ratios

$$\Delta I/I_0 = \Delta G/G_0 = \Delta R/R. \quad (3)$$

In addition, presentation of data in this form permits comparisons of sensitivity between cells of different area and grid spacing.

In order to utilize the above equations, it is essential that the photo-sensitive area of the cell be uniformly and completely illuminated. These conditions have only been approximated in measurements requiring the use of the monochromator by employing a spot size of diameter equal to the length of the side of the square sensitive surface. The effect of spot size on cell response for constant light input is illustrated by Fig. 8.

### C. Dark Current and White Light Response

The temperature dependence of the dark conductance of oxidized thallosulfide is typical of

that of a semiconductor,  $G_0$  decreasing exponentially with the reciprocal of the absolute temperature over a wide range (Fig. 9, Eq. (4)).

$$G_0 = ae^{-U/kT}, \quad (4)$$

$a$  = constant,  $U$  = activation energy.

Owing to the high temperature coefficient of the dark current, the accuracy of light response measurements is limited at very low and very high light intensities; but, as is evident from Fig. 10, only at very low levels of illumination does the photo-current increase proportionally to the light input. At higher light intensities the response deviates considerably from linearity. This behavior explains the previously noted observation (Fig. 8) that the output decreases when the light is concentrated on a smaller spot.

### D. Spectral Response and Quantum Yield

The spectral response characteristic of the thallosulfide cell (Fig. 11) varies with the illumination level because of the non-linearity of the cell. In addition to the photo-current,  $\Delta I$ , the quantum yield,  $\eta$ , is plotted in Fig. 11, assuming that every incident light quantum is absorbed and contributes to the photo-effect:

$$\eta = \frac{\text{photo-electrons}}{\text{incident quanta}} = \frac{(1.24)(\Delta I)}{(\lambda)(F)}. \quad (5)$$

( $\Delta I$  = photo-current in  $\mu$  amp.,  $F$  = light input in  $\mu$  watts,  $\lambda$  = wave-length in microns). Because of this assumption, the calculated quantum yield will be lower than the true yield; nevertheless, the former surpasses unity by a large margin.

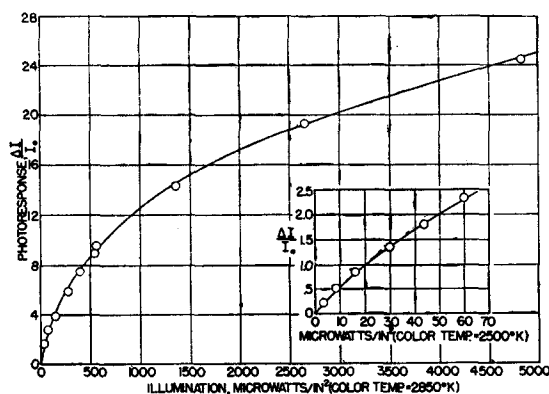


FIG. 10. White light response as a function of illumination.

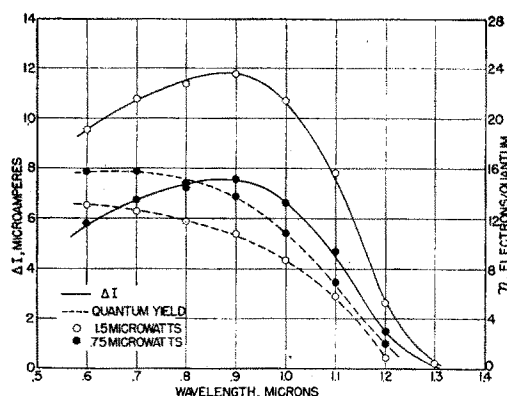


FIG. 11. Photo-current and quantum yield as function of wave-length for two light intensities. ( $R_0=2.5$  meg.;  $V=22.5$  v.)

This result establishes beyond question that the photo-currents observed in thallosulfide cells are the result of a secondary photo-effect.

Plots of light response *vs.* intensity for different wave-lengths (Fig. 12) are similar in shape and, in fact, can be combined into a single curve by multiplying the  $\mu$ -watt scale of each plot by a characteristic factor,  $a$ . For example, in Fig. 13 all curves have been converted into the  $0.9\mu$  characteristic by employing the  $a$  factors tabulated in the figure. It appears that a plot of the different  $a$  factors against wave-length represents a relative spectral sensitivity curve for constant light current output.

$$a = \frac{\eta_{\mu} \lambda_{\mu}}{\eta_{0.9} \lambda_{0.9}} \quad (6)$$

This curve also corresponds to the relative spectral sensitivity curve that would be obtained at very low illumination levels within the linearity range.

Similarly, all plots of light response *vs.* intensity for different temperatures and for a given wave-length (Fig. 14) can be combined into a single one by multiplying the  $\mu$ -watt scale by factors  $b$  (Fig. 15). Again a plot of  $b$  against temperature indicates how the response varies with temperature for a constant light current output.

## VI. THERMOELECTRIC STUDIES ON THALLOUS SULFIDE

The type of electronic conduction prevailing in semiconductors can be determined from the sign

of the thermal e.m.f. Since the mobile charge carriers stream from the hot to the cold junction, excess conductivity charges the cold junction negative, while the migration of holes produces the opposite polarity.

### A. Apparatus and Procedure

Measurements\* of the thermovoltage coefficient were made on a number of thin films of thallosulfide in various stages of oxidation. Figure 16 shows the special type of cell used in these measurements. The two tungsten electrodes were ground flat and sealed into the Pyrex bulb through glass arms, which could be filled during the experiments with liquids of the desired temperature difference ( $\sim 60^\circ\text{C}$ ). The faces of the electrodes were covered with aquadag, which was subjected to the standard outgassing procedure before thallosulfide was evaporated onto the

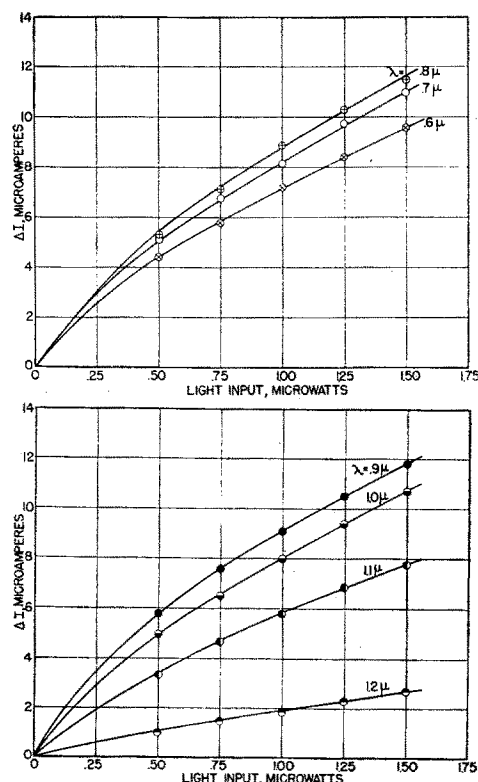


FIG. 12. Photo-response *vs.* light intensity and wave-length. ( $R_0=2.5$  meg.;  $V=22.5$  v.)

\* The thermoelectric study was begun and the majority of these measurements were made by G. Oster, the remainder by R. B. Speed.

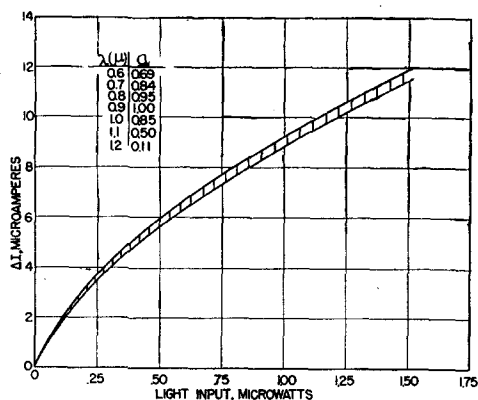


FIG. 13. Conversion of wave-length curves into the  $0.9\mu$  characteristic.

upper half of the glass bulb. Thermovoltages were measured by means of a feedback amplifier of high input impedance.<sup>18</sup>

### B. Results

Thallous sulfide sample No. 1, which was known to be slightly pre-oxidized (Section I), exhibited defect conductivity after evaporation and the sign of the thermal e.m.f. did not change on further oxidation. However, sample No. 2, which was completely free of oxygen, manifested excess conductivity after evaporation. With increasing oxidation of this sample the conductivity fell, the photo-sensitivity rose, and the thermovoltage went through zero and reversed sign as is shown in Fig. 17. Defect conductivity is represented in the figure by a positive sign of the thermal-e.m.f. coefficient.

A minimum in the conductivity characteristic did not accompany the change in sign of the thermo-e.m.f., in contradistinction to a case like  $\text{PbS}$ <sup>19</sup> where the material is an insulator at the stoichiometric composition and a defect or excess conductor in the presence of a defect or excess of the metallic constituent. Hence, if sample No. 2 does not contain an excess of either of its constituent elements, the data seem to indicate that thallous sulfide is both an excess and defect conductor and that oxidation reduces the originally dominating excess conductivity to a higher degree than the hole conductivity, thus producing a reversal of sign.

<sup>18</sup> S. Roberts, Rev. Sci. Inst. **10**, 181 (1939).

<sup>19</sup> H. Hintenberger, Zeits. f. Physik **119**, 1 (1942).

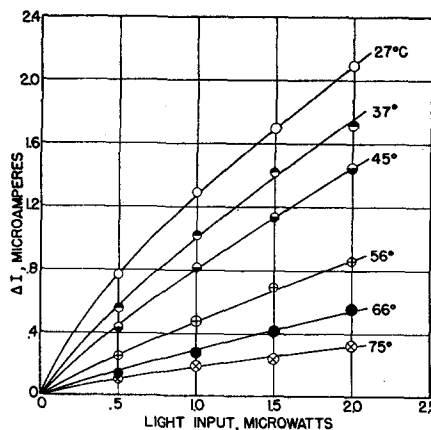


FIG. 14. Effect of temperature on photo-response. ( $\lambda = 0.8 \mu$ ;  $V = 22.5$  v.)

Illumination of an oxidized layer resulted in a slight increase in the magnitude of the positive thermovoltage, indicating that light increases the defect conductivity of the material.

Thermal e.m.f. measurements have previously been made by Hochberg and Sominski<sup>20</sup> on thallium sulfide samples subjected to a variety of heat treatments in air. We agree with these authors that high resistant  $\text{Tl}_2\text{S}$  shows defect and low resistant material shows excess conductivity; but their conclusion that pure  $\text{Tl}_2\text{S}$  is a hole conductor, changing to an excess conductor on oxidation, is contrary to our findings.

### VII. TRANSMISSION AND REFLECTANCE MEASUREMENTS ON THALLOUS SULFIDE LAYERS

Transmission measurements between 3000 and 8500 Å\* were made on several evaporated films of thallous sulfide prepared in cells of normal construction but lacking gridworks. Typical data obtained on very thin films are shown in Fig. 18. It is apparent that the absorption increases at shorter wave-lengths.

Measurements of transmission and reflectance between 4000 and 7000 Å\*\* were made using a special absorption cell, fabricated from "Precision Bore" tubing of square cross section and containing a  $\text{Tl}_2\text{S}$  layer of standard thickness (5000 Å). The transmission proved to be less than

<sup>20</sup> B. M. Hochberg and M. S. Sominski, Physik. Zeits. Sowjetunion **13**, 212 (1938).

\* A Hilger Spekker photometer was employed in these measurements.

\*\* A Hardy color analyzer was used in this work.

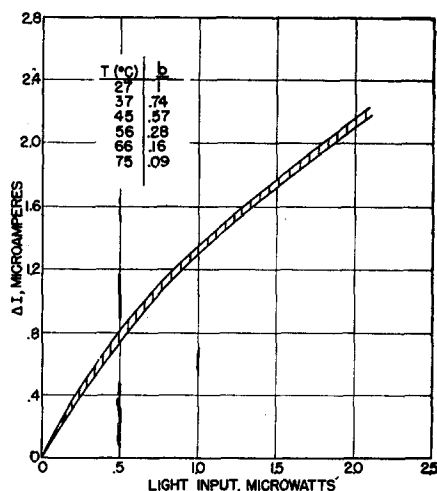


FIG. 15. Conversion of temperature curves into the 27°C characteristic.

0.1 percent and the reflectance  $25 \pm 1$  percent over this spectral range.

From some additional data obtained between 8000 and 12,000 Å\*\*\* on layers of standard thickness, it appears that there is a peak in the transmission curve at about  $1.0\mu$  and that about 10 percent of the incident light is transmitted at this wave-length.

Over the entire spectral range investigated the presence of oxygen does not seem to alter materially the shape of the transmission curve.

#### VIII. RESPONSE TO FLASHES OF SHORT DURATION

In order to determine the build-up and decay characteristics of the photo-current, an investi-

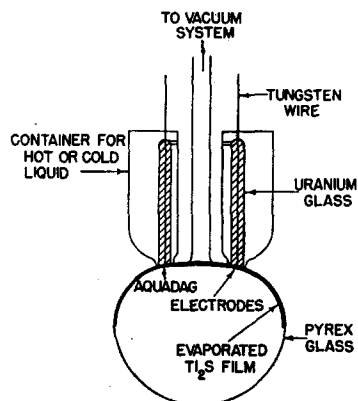


FIG. 16. Cell for thermo-e.m.f. determination.

\*\*\* The Gaertner monochromator was employed for this purpose.

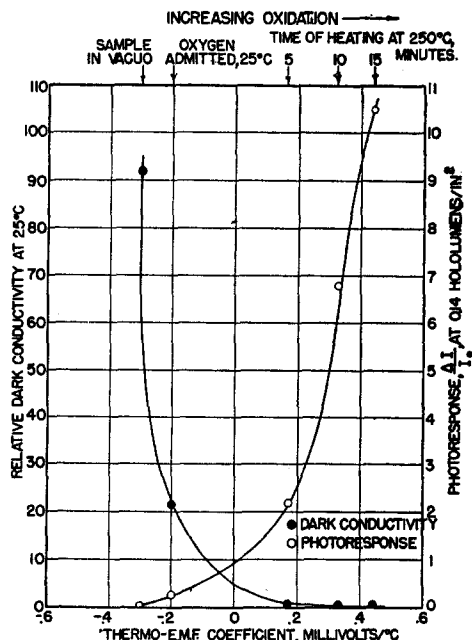


FIG. 17. Relation between dark conductivity, photo-response, and thermo-e.m.f. coefficient with increasing oxidation.

gation was made of cell response to light flashes of extremely short duration.

#### A. Equipment and Procedure

The incandescent lamp source mounted in front of the monochromator slit was replaced by a discharge tube of the Edgerton type which could be flashed for approximately  $3 \times 10^{-6}$  second by a condenser discharge.

The photo-cell was connected in series with a battery and load resistance in the usual manner. The load resistance was coupled to a cathode follower unit with low input capacitance, approximately  $5 \mu\text{f}$ , to eliminate frequency distortion, and the cathode follower output was amplified by a single-stage a.c. amplifier.\* The output of this amplifier was further amplified by the Y axis amplifier of a DuMont Type 208 oscilloscope, and the trace, which appeared on the screen of a 5LP1 DuMont cathode-ray tube, was photographically recorded. In order to expand the time scale, a multiple sweep arrangement was used which was a modification of the circuit described by Richter.<sup>21</sup>

\* The electronic circuits were constructed by M. Haugen.

<sup>21</sup> W. Richter, Electronics 17, No. 9, 128 (1944).

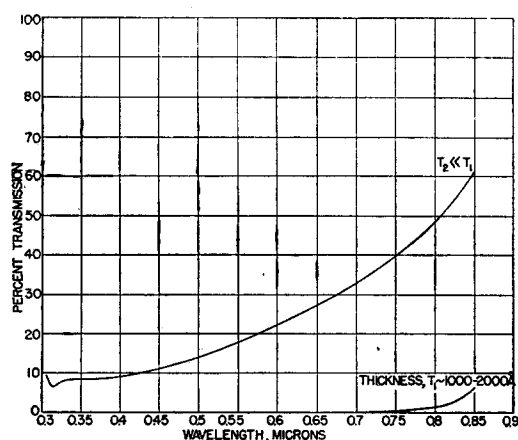


FIG. 18. Transmission of thallos sulfide layers.

For our analysis it was desired to determine the change in conductance as a function of time. In order to simplify the interpretation of the various photographed patterns, it was necessary to select load resistance values,  $R_L$ , so as to obtain proportionality between output voltage (across  $R_L$ ),  $\Delta E$ , and change in cell conductance,  $\Delta G$ . Since it can be shown that

$$\Delta E = R_L \Delta I = \frac{R_L \Delta G (R_0 - \Delta R) I_0}{G_0 (R_0 - \Delta R + R_L)}, \quad (7)$$

it is apparent that in order to obtain proportionality between  $\Delta E$  and  $\Delta G$  it is necessary that  $R_L \ll R_0 - \Delta R$ . This condition was fulfilled in the majority of our experiments by employing a load resistance of 10,000 ohms. At extremely low light intensities, however, it was possible to use a load resistance as high as 200,000 ohms.

The flash response of the thallos sulfide photo-cell was studied as a function of voltage, wave-length, light intensity, and temperature. In addition, cells of different resistance and oxidation states were compared under closely similar conditions.

The intensity of the flashes was controlled by altering the slit widths of the monochromator. The intensity of a single flash could not be accurately duplicated, however, since the discharge was not completely reproducible in intensity and location. Nevertheless, a measure of the intensity could be had by determining the peak value of  $\Delta G/G_0$  from an examination of the

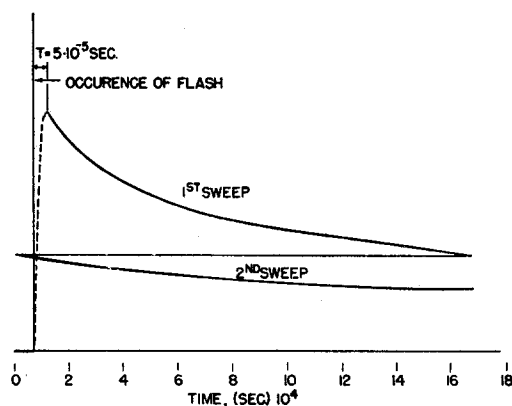


FIG. 19. Oscillograph trace of response to flash.

photographed pattern and from the known dark conductance. The relative intensities of the flashes were varied over a range of the order of 3000:1, the lowest intensity being limited only by cell and circuit noise.

For the temperature measurements the electrically heated oven was mounted inside the same shielded container as that enclosing the cathode follower and amplifier circuits. The small capacitance of the cell, about 10  $\mu\text{mf}$ , increased only by about 50 percent in the oven mount.

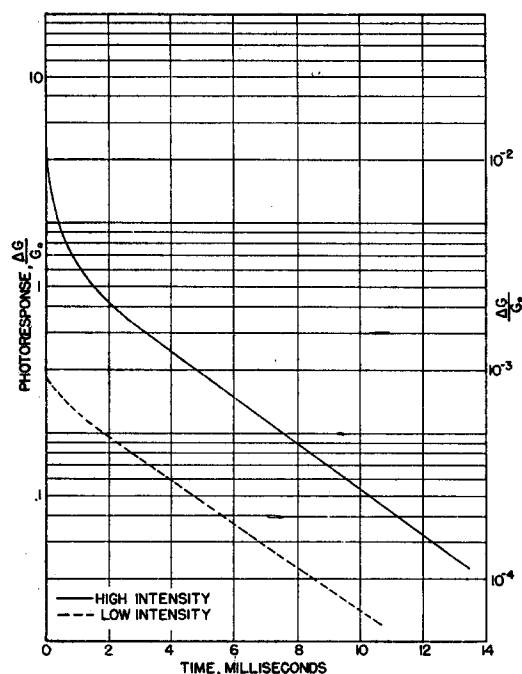


FIG. 20. Decay characteristics for two light intensities.

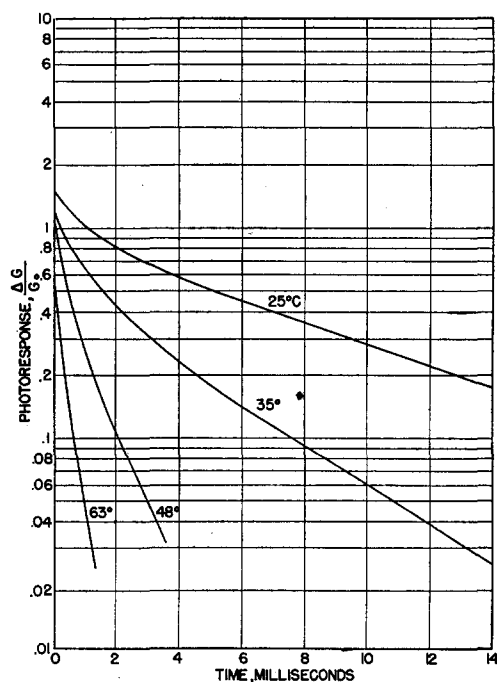


FIG. 21. Decay characteristic as function of temperature.

### B. Results

All cells thus far investigated exhibit a response characteristic typified by Fig. 19. After the occurrence of the light flash, the photo-current builds up in about  $5 \times 10^{-8}$  second to its maximum value; its decay with time is exponential save for the very beginning of the curve. This can be readily seen in a plot of the photo-response on a logarithmic scale against time (Fig. 20), where the slope is steepest initially and rapidly decreases to a constant value,  $\kappa$ .

The voltage applied to the cell and a change in wave-length of the monochromatic light flash between 0.6 and  $1.1\mu$  have no effect upon the shape of the decay characteristic.

Light intensity and temperature, on the other

TABLE IV. Peak flash response *vs.* temperature.

Peak $\Delta G/G_0$	$T^\circ\text{C}$
1.45	25
1.17	35
1.05	48
0.67	63
0.24	76
0.11	85

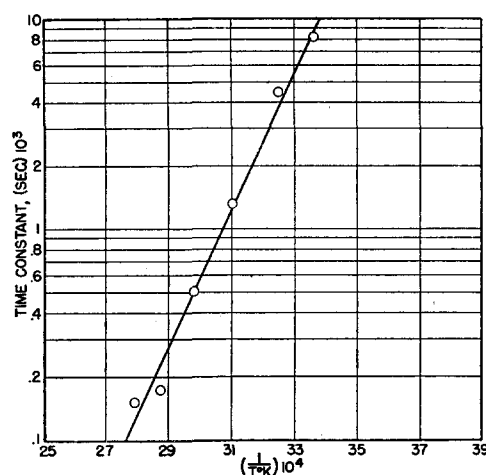


FIG. 22. Temperature dependence of the time constant.

hand, have a pronounced effect. With increasing intensity the initial slope of the log plot becomes progressively steeper while the slope of the linear portion of the curve remains the same (Fig. 20) within the limits of error of about  $\pm 10$  percent. With increasing temperature, although the time of rise remains unchanged, the cell decay becomes progressively more rapid and the peak in the response curve falls (Fig. 21). The variation of peak response with temperature is a linear function as the data of Table IV show. The time constant,  $1/\kappa$ , of the exponential portion of the decay curve increases exponentially with the reciprocal of the absolute temperature (Fig. 22). In the one instance where reliable measurements are available, the value of the activation energy (0.65 electron volt) obtained from the slope of this curve is slightly larger than the activation energy,  $U$  (0.54 electron volt), determining the dark current dependence on temperature.

On comparing sensitive cells of different resistances and oxidation states (Table V), it appears that the time constant,  $1/\kappa$ , increases in a very general way with decreasing cell resistance, although no correlation between time constant and composition can be seen. No relationship has been found between the magnitude of the peak in the response curve and  $1/\kappa$ ,  $R_0$ , or composition; the data are not included in the table as all measurements were not made at the same intensity level.

On comparing insufficiently oxidized cells at

the same light intensity and applied voltage (Table VI—cell No. 4 of high sensitivity included as a typical end member of the series), it can be seen that the peak yield increases rapidly with oxygen content while the time constant remains

TABLE V. Time constant *vs.* dark resistance and composition of sensitive cells.

Cell No.	$(1/\kappa)10^3$ , sec.	$R_0$ , megohms*	Composition, mole $O_2$ /mole $Tl_2S$
114B	1.3	840	0.69
2A	0.53	450	0.578
18A	0.33	322	0.307
60B	0.80	225	0.16
166B	10.2	140	0.36
138B	1	72.5	0.21
4A	2.6	51	0.25
6A	2.6	26.5	0.339
84B	8.7	22.5	0.39
66B	4.2	20.4	0.16
40B	5.4	15.0	0.39
168B	5.2	10.5	0.30
86B	11	10.0	0.16
54B	21	5.0	0.39
50B	28	1.6	0.39
136B	56	1.05	0.38
116B	37	0.15	0.16

\* The differences in values of  $R_0$  from those reported in Table II are the result of long aging.

relatively unchanged. However, the time constants of cells 59A and 5A are considerably smaller than Table V would lead one to expect for cells of such low resistance.

TABLE VI. Peak yield, time constant, dark resistance *vs.* composition of insensitive cells.

Cell No.	Peak $\Delta G/G_0$	$(1/\kappa)10^3$ , sec.	$R_0$ , megohms	Composition, mole $O_2$ /mole $Tl_2S$
59A	$1.5 \times 10^{-5}$	1.7	0.018	0
5A	$3.23 \times 10^{-3}$	1.2	0.132	0.119
4A	$3.79 \times 10^{-1}$	2.6	51	0.25

TABLE VII. Frequency response.

Cell No.	$1/\kappa$ , sec.*	Frequency, cycles/sec.	30	90	180	360	720
50B	$3.6 \times 10^{-2}$	Signal,** db	104	98	93	86	81
18A	$3.3 \times 10^{-4}$	Signal, db	58	58	58	56	53

\* From flash response data.

\*\* Without filter; reference level  $0.1\mu$  volt = 0 db.

## IX. FREQUENCY RESPONSE

The relative response to modulated light as function of frequency varies widely for different photo-cells as indicated by the data of Table VII. Cells possessing very short time constants, which are not common, exhibit good relative response with frequency over the range investigated. The quantitative relation between frequency response and time constant will be given in connection with a general theoretical discussion to be published in a subsequent paper.