A COMPARATIVE STUDY OF THE LIGHT-SENSIBILITY OF SELENIUM AND STIBNITE AT 20° C. AND − 190° C.

BY D. S. ELLIOTT.

IT is a well-known fact that selenium experiences a decrease of resistance when exposed to light under the proper conditions, and several explanations for this fact have been offered. It was suggested by Pfund[1] that the conduction in selenium is electronic and that the increased conductivity may be accounted for on the assumption that the absorbed light sets electrons in resonance resulting in their expulsion outside the atoms. This would increase the number of electrons available for carrying the current and hence increase the conductivity.

Among the facts that can be marshalled in support of the electronic hypothesis, the most important are these:

1. As shown by Thomson in his "Conduction of Electricity Through Gases," the current through an ionized gas is proportional to the square root of the energy of the ionizing agent, provided the ionization has reached a steady state. The same law has been shown by Pfund[2] and Nicholson[3] to hold for selenium for unlimited exposures to radiation from $\lambda = 230\mu\mu$ to $\lambda = 900\mu\mu$ and for X-rays.

2. Another general property of electronic conduction is the absence of polarization. A number of investigators[4] have definitely established the fact that normal selenium cells show no polarization. This proves that the conduction is not electrolytic.

3. The retention of light-sensibility at the temperature of liquid air is also evidence for the electronic hypothesis. This property of selenium is clearly shown by the experiments of Pochettino,[5] Miss McDowell[6] and the author.

4. All light-sensitive substances show the "voltage effects"; *i. e.*, Ohm's law is not obeyed. Ries,[7] Adams[8] and Luterbacher[9] have shown

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[1] Pfund, PHYS. REV., 28, 1909, p. 324.

[2] Pfund, PHYS. REV., XXXIV., No. 5, May, 1912.

[3] Nicholson, PHYS. REV., Vol. III., Jan., 1914.

[4] Ries, "Electrical Properties of Selenium," p. 53. Pfund, Phys. Zeit., 10, 340, 1909.

[5] Pochettino, Rend. R. Accad. dei Linc., Sec. 5, Vol. II., p. 286.

[6] McDowell, PHYS. REV., 31, p. 524, 1910.

[7] Ries, Phys. Zeit., 12, p. 480 and 552, 1911.

[8] Adams, Proc. Roy. Soc., 23, 1875.

[9] Luterbacher, Ann. d. Phys., 33, 1392, 1910.

that the specific resistance of selenium decreases with an increase of voltage, and also decreases as the current continues to pass through the cell.

Object of Investigation.—As the information on selenium at liquid air temperature was not as complete as might be desired, it seemed advisable to investigate this further. The particular object of the investigation, however, was to examine other light-sensitive substances and determine whether or not they showed behavior similar to selenium at 20° C. and – 190° C. Most of the observations have been confined to stibnite.

Cells.—In order to carry out this investigation, it was first necessary to prepare cells which would meet the extreme demands necessitated by this temperature variation. It soon became evident that selenium cells prepared in the usual way would not suffice, as it was found that after a cell had been subjected to the temperature of liquid air and was brought back to 20° C., its behavior was markedly different. After some experimenting, cells were constructed according to the following design which is due to Professor Pfund. This cell has proven so satisfactory that it seems well to describe it in some detail.

Selenium Cells.—Amorphous selenium was first cast into discs about 1.5 cm. in diameter and 1.5 mm. thick. They were sensitized in the usual way, being maintained at a temperature of 200° C. for six hours and then cooled rapidly to room temperature. The discs were then ground smooth on crocus cloth, after which silver tape electrodes were fastened on with celluloid. A film of gold was next deposited by cathode sputtering, and finally the gold was removed along a narrow line like a grid as shown in Fig. 1. Attention is called to the four shallow pools of celluloid shown. Besides strengthening the construction these provide a smooth transition from the selenium to the upper surface of the silver tape. In this way fractures of the gold film were avoided. The time required for the deposition from the insertion of the cell to its removal did not exceed twenty minutes; but as a matter of fact, the selenium was covered with a protective layer of gold within six minutes. No

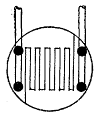

Fig. 1.

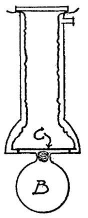

Fig. 2.

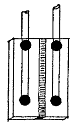

Fig. 3.

deleterious action due to mercury vapor could be detected. The cell was finally enclosed in a glass tube similar in design to Fig. 2. Bulb *B* was filled with calcium chloride and the constriction leading to the upper chamber loosely plugged with cotton. The cell "*c*" was fastened with sealing wax in this upper chamber, the end of which was closed by a glass plate. The vessel was also provided with a side tube for exhausting by means of an aspirator, a phosphorus pentoxide tube being inserted between cell and aspirator during the process.

Stibnite Cells.—Stibnite cells were made and mounted in essentially the same way as the selenium cells. Starting out with crystals of stibnite[1] (Sb_2S_3) and using the cleavage surfaces, in some cases gold was deposited over the whole surface and afterwards removed along a line by scratching; in other cases a protective layer of tin-foil about 0.5 mm. wide was placed along the middle of the surface before deposition. This tin foil was afterwards removed disclosing a strip of clean cleavage surface which could be exposed to the light. Fig. 3 is a picture of a stibnite cell.

Apparatus.—The arrangement of apparatus is shown in Fig. 4. The source of illumination was a Nernst lamp *L*; a spectrometer of the Wadsworth type broke up the radiation into quasi-monochromatic light focused in the plane of slit S_2; the light could then follow one of two paths depending upon whether the right-angle prism *P*, hinged at *H*, was raised or lowered. With the prism *P* swung out of the way, the light was focused by the lens L_2 on a sensitive thermal junction. This system, constructed according to his latest design,[2] together with a sensitive galvanometer, was built by Professor Pfund and kindly placed at my disposal. Its sensibility was such that a candle at a meter's distance gave a deflection of 30 mm. With the prism *P* down, the light was diverted downward upon cell "*c*" which was inserted in a Dewar flask. The amount of glass in the path of the beam over both paths was approximately the same, and it might be said at this point that in carrying out any set of experiments to determine the effect of temperature or anything

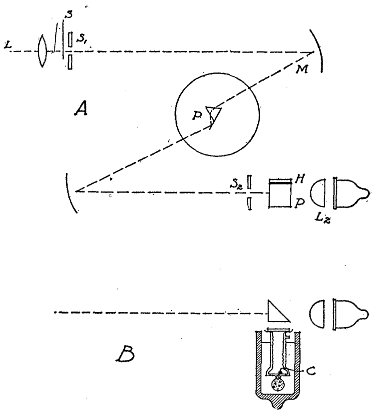

Fig. 4.

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[1] The crystals of stibnite were generously furnished by Dr. W. W. Coblentz of the Bureau of Standards.

[2] Pfund, Phys. Zeit., XIII., 870, 1912.

else, that particular factor could be varied alone without disturbing the cell in any way. Results obtained are therefore strictly comparable.

In measuring increased conductivity the usual method was employed. Diagram 5 shows the arrangement. In some cases a counter E.M.F. was introduced at the galvanometer terminals to annul the "dark deflection," and when the increased conductivity was too large, a shunt R was introduced to cut down this deflection. In some cases both the counter E.M.F. and the shunt were unnecessary. Both this galvanometer (sensibility 1.5×10^{-8} amperes) and a device for exposing for the desired time, were placed in an adjoining room. In general, exposures of ten seconds were taken, and an interval of three or four minutes elapsed between readings.

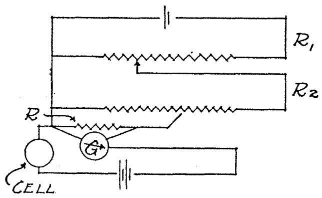

Fig. 5.

Sensibility Curve. Selenium 20° C.—In these observations, cells of the new design were used. Strictly speaking the sensibility of a cell is the ratio of the two quantities—the change in resistance per unit energy illumination, and the dark resistance. The quantity used in plotting these curves is proportional to this. The galvanometer deflection corresponding to a certain value of incident energy was first obtained. The deflection corresponding to a particular value of energy taken as unity could then be calculated from the relation $D = KE^{\beta}$ where D is the galvanometer deflection, K a constant, E the incident energy and β another constant. For unlimited exposures, Pfund and Nicholson have shown that $\beta = 0.5$, and this is the value used in applying the formula unless definitely stated otherwise. Attention is called to the fact that actual observations near the sensibility maximum were taken for energies which do not vary appreciably from the value of energy taken as standard. This was accomplished by adjusting the voltage on the Nernst lamp and the width of the slit S_1. In this way all possibility of vitiation of the results by the assumption of any law connecting galvanometer deflections and energy was obviated. Curve I. gives the sensibility curve for selenium cell D, temperature 23°.5 C., 120 volts.

Sensibility Curves of Selenium at − 190° C.—In taking these curves the Dewar flask was filled with liquid air and replaced about the cell. This adjustment could be effected without disturbing the rest of the apparatus. Sufficient care was taken to see that the flask remained well filled with liquid air. By means of a funnel arrangement, not shown in the drawing, the supply of liquid air could be replenished without withdrawing the flask, so that the cell remained undisturbed in liquid air throughout the experiment. In all recorded experiments the cell was brought to this low temperature very gradually, and throughout the procedure the conductivity was observed to fall very rapidly until it became barely perceptible. Observations of Pochettino[1] and Miss McDowell[2] also show that the resistance of selenium at liquid air temperature is enormously great.

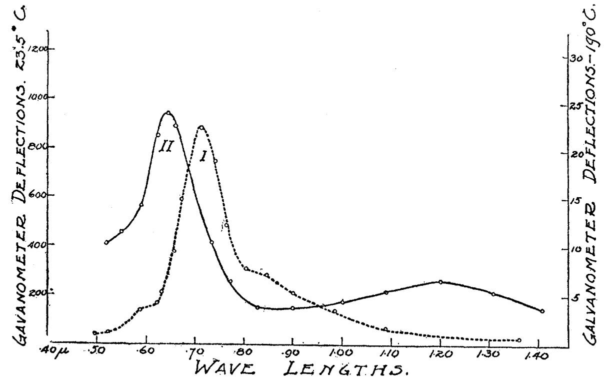

Fig. 6.

In the early part of the work some experiments were carried out to determine whether or not the ratio of the increased conductivity to the original conductivity—$\Delta c/c$—was independent of the temperature for any one wave-length. Fig. 7 gives the arrangement of the apparatus for this part of the work. The circuit containing the cell c and a storage battery B was completed through S the secondary of a transformer; the primary coil P was connected to a sensitive galvanometer G. Exposures of 0.2 second were obtained by means of a pendulum also shown in the drawing, and a device was fixed to the pendulum so as to break the primary circuit slightly before the exposure of 0.2 second was completed. In some cases $\Delta c/c$ was independent of the temperature, in other cases this ratio increased with temperature, while in still other cases it decreased as the temperature was raised. In all cases, however, the results were of the same order of magnitude. A possible explanation based on a change of optical properties is suggested from a consideration of the change in sensibility curves for the two temperatures. The striking fact, however, is that the light becomes

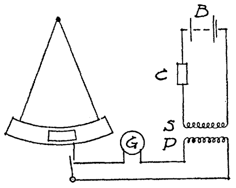

Fig. 7.

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[1] Pochettino, Rend. R. Accad. dei Linc., Sec. 5, Vol. II., p. 286.

[2] McDowell, Phys. Rev., 31, p. 524, 1910.

effective at the temperature of liquid air just as rapidly as at ordinary temperatures, while the recovery for the lower temperature is very much slower.

A typical sensibility curve for selenium at – 190° C. for a ten-second exposure is shown in Curve II. In making all observations at liquid air temperature, the cell was afterwards brought back to room temperature to determine whether or not the first readings could be reproduced. This is the reason why early observations on cells of standard design were discarded as worthless. With the new design no difficulty was experienced.

Voltage effects were detected at liquid air temperature.

From a comparison of Curve I. and II. the following conclusions seem to stand out most pronounced: Lowering the temperature of selenium from 20° C. to – 190° C. causes

1. An extension of the range of sensibility from 0.9 μ to 2.0 μ approximately.
2. A shift of the sensibility maximum towards the region of shorter wave-lengths by about 600 A.U.

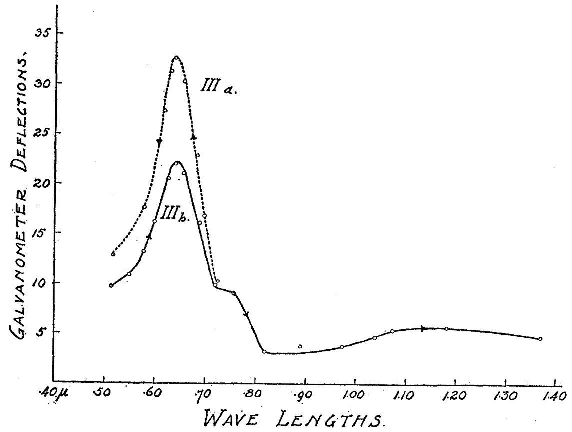

Fig. 8.

The position of the sensibility maximum is unaffected by the voltage effect and the direction of progression through the spectrum. This is shown by Curves III_a and III_b which refer to selenium at – 190° C. Curve III_b as indicated by the arrow is plotted from readings taken through the spectrum from shorter to longer wave-lengths, Curve III_a refers to the same cell, readings being taken in the reverse order. During the course of the readings the conductivity was observed to increase appreciably although the temperature must have remained constant. The position of the sensibility maximum, however, is unaffected.

Stibnite.—The light sensitive property of stibnite (Sb_2S_3) was discovered by Jaeger[1] in 1907, and Ries[2] showed later that this substance exhibits the same voltage effects as selenium. It was decided to investigate this substance further, using as the mode of attack the sensibility curves obtained under various conditions. The cells were mounted in the same way as the selenium cells previously described.

Law Connecting Energy and Deflection. Room Temperature.—In investigating this point a rotating sector was placed before the spectrometer slit S_1 (see Fig. 4). The disc was so constructed that by sliding the motor along a pair of ways, full, one half, or a quarter energy was allowed to fall on the slit, and the resulting galvanometer deflections could be obtained. The accompanying table is representative of this part of the work.

Exposure 10 sec. 110 volts. 21° C.

Wave-lengths.	D_1=Galv. Defl. Full Energy, Mm.	D_2=Galv. Defl. ½ Energy, Mm.	D_3=Galv. Defl. ¼ Energy, Mm.	β Calc. from D_1 and D_2.	β Calc. from D_1 and D_3.
0.642μ	9	6.2	4	0.54	0.58
.670	16	11	7.7	0.54	0.53
.685	27.5	19.3	13.7	0.51	0.53
.700	59	39	26.7	0.59	0.57
.740	137.5	95.1	66.7	0.53	0.52
.768	86.75	54.5	35.8	0.67	0.64
.800	39.5	23	15.1	0.78	0.69
.873	7	3	2	1.02	0.92

Exposures of ten seconds were made, and the relation $D = KE^{\beta}$ was assumed to hold between galvanometer deflection D and the energy E. Having two values of D as well as the ratio of the corresponding energies, the value of β is easily calculated. It will be observed from the foregoing table that the value of β for shorter wave-lengths is in general less than for the longer wave-lengths. This is similar to what we find in selenium. The obvious explanation is that a greater time is required for equilibrium for the longer wave-lengths. For the same reason the value of β for all wave-lengths is too large. For exposures sufficiently long enough to ensure equilibrium, it is safe to say that the square root law holds for stibnite. In other words, stibnite obeys the law $D = KE^{\beta}$ where D is the galvanometer deflection, K is a constant, E the energy and $\beta = 0.5$ approximately.

Sensibility Curve for Stibnite at Room Temperature.—Two specimen sensibility curves will be given in this connection. Both refer to the

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[1] Jaeger, Proc. Roy. Acad. Sci. Amsterdam, 9, 808, 1907.

[2] Ries, Ann. d. Phys., 36, 1911, p. 1055.

same stibnite cell—cell "*A*," which had a scratched surface. The first observations were taken by exposing the cell until equilibrium was reached. Owing to the voltage effect in stibnite the galvanometer never came absolutely to rest, but equilibrium was considered to have been reached when the galvanometer moved less than 1 mm. per minute. After each reading the cell was allowed to "soak" back approximately to its original conductivity before the next reading was taken. Intervals between readings amounted in some cases to as much as thirty-five minutes. Curve IV. gives these results. Curve V. refers to the same cell, readings being taken for exposures of ten seconds. All other conditions were practically the same. Comparing Curves IV. and V., we see that for unlimited exposures the sensibility maximum lies further in the red. An explanation of this fact is that while equilibrium is approximately reached for the shorter wave-lengths in ten seconds, such is not the case for the other end of the spectrum. The effect of longer exposures is therefore to increase the ordinates corresponding to longer wave-lengths, leaving the short wave-lengths practically unaffected. Consequently the maximum shifts towards the longer wave-lengths.

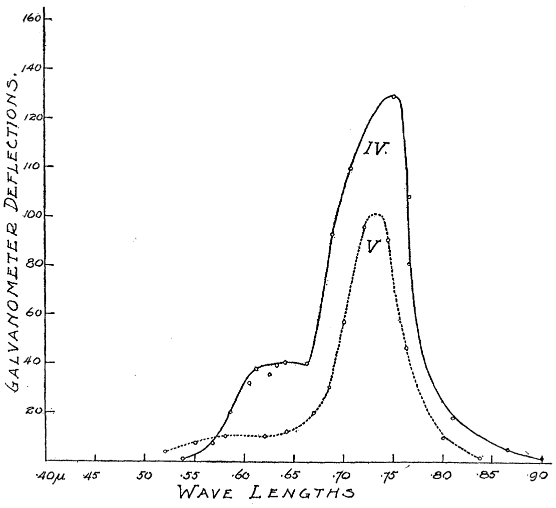

Fig. 9.

Voltage Effects.—As other investigators[1] have already observed, stibnite shows the voltage effects. The specific resistance decreases with the voltage; and for the same voltage, the resistance decreases with time. Like selenium, stibnite cells do not regain their original conductivity

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[1] Ries, Ann. d. Phys., 36, 1655, 1911.

immediately but require time. Compared with selenium, however, this return is much more rapid.

Stibnite at the Temperature of Liquid Air.—Sensibility curves were obtained at this temperature, and the law connecting galvanometer deflections and energy investigated. A cursory examination seemed to indicate that at this temperature the square root law held for equilibrium exposures, but as it was proposed to use an exposure of ten seconds for the sensibility curves, the law connecting energy and deflections was investigated under these conditions. The data referring to this part of the work follows:

Stibnite Cell "*D.*" Temperature − 190° C.
Voltage 120. Exposure 10 sec.

Wave-lengths.	D_1 = Galv. Defl. Full Energy. Mm.	D_2 = Galv. Defl. Half Energy, Mm.	β Calc. from D_1 and D_2.
0.577	13.65	8.3	0.71
0.616	17.25	10.14	0.74
0.735	21.6	12	0.85
0.813	30.9	17.97	0.78
		Mean value	0.77

Sensibility Curves of Stibnite at − 190° C.—A number of experiments were carried out on different cells of both the scratched and the unscratched variety. Curve VIII. is a typical curve. Although the value

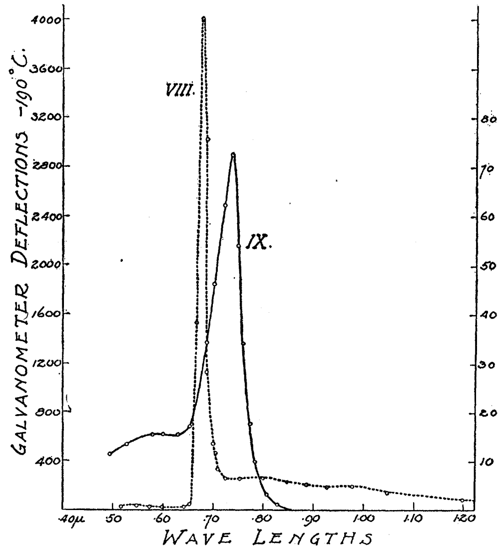

Fig. 10.

of β used in reducing the deflections to equal energies was 0.77, a calculation showed that there would be no sift of the position of the sensibility maximum for values of β ranging from 0.5 to 1.0. Curve IX. refers to the same cell at room temperature.

From a comparison of Curves VIII. and IX., these two conclusions stand out most prominently: Lowering the temperature of stibnite from 20° C. to − 190° C. causes:

1. Extension of the region of sensibility to 2 μ approximately.
2. Shift of the sensibility maximum towards the region of shorter wave-lengths by about 600 A.U.—approximately the same as for selenium.

Anomalous Stibnite Cells.—In addition to the general characteristics enumerated above, two cells—stibnite cell "*B*" and stibnite cell "*X*," exhibited some surprising properties. A preliminary test with an incandescent lamp indicated that these cells were quite normal, but with monochromatic light some unexpected properties were found. For certain regions of the spectrum these cells were photo-negative, while for longer wave-lengths they were photo-positive. The performance of stibnite cell "*B*" is given in the following table:

Stibnite Cell "*B*." Temperature 20°.5 C.
Voltage 20. Exposure 10 secs.

Wave-lengths.	E_1 = Energy Defl., Mm.	D_1 = Galv. Defl., Mm.	E_2 = Energy Defl., Mm.	D_2 = Galv. Defl., Mm.
0.5035μ	11.5	− 8	2.0	− 5
0.5302	20.5	−10	3.25	− 5
0.5602	40	− 7.5	7	− 7
0.5936	79	−10	14.5	− 7.4
0.634	160.5	− 5.2	31	− 5
0.657	219	0	47.5	0
0.695	229	+16	54	+ 9
0.724	234	+18	57.5	+10.5
0.767	198	+19.5	54.5	+ 4
0.806	185			

It seems well to mention that whenever the deflection was negative, an additional negative deflection was observed immediately after the light was turned off. Just what the explanation is, it is impossible to say, but it is certain that the effect is in the cell itself and is not due to external electrical influences. Glancing at the table, it is seen that no deflection is recorded for $\lambda = 0.657\ \mu$. The inference must not be drawn from this that the galvanometer remained entirely quiescent. As a matter of fact there was first a positive deflection of 1.5 mm., followed immediately by an equal negative deflection. No simple relation was found connecting energy and deflection. It is evident that we are dealing here with the superposition of two effects. A superficial study shows that if the law $D = KE^\beta$ does apply, the values of β for the positive and the negative effects are entirely different.

At the temperature of liquid air this cell showed the maximum in the usual position. At this temperature the negative effect was entirely absent; the range of sensibility had been extended considerably, positive deflections being recorded from 0.48 μ to 2.5 μ. Returning to 20° C. the cell was found to be light negative again. The writer hopes to investigate photo-negative selenium cells prepared according to Brown's process,[1] to see whether or not this photo-negative property is fundamental in character.

Stibnite cell "X" when first prepared showed this photo-negative property even more strikingly than cell "B." Twenty-four hours later this had entirely disappeared and the cell though unsteady was normal in its behavior. The transient character of this photo-negative property as indicated by cell "X" is controverted by cell "B" fully described above. At the time of writing cell "B" which is a month old still retains its photo-negative characteristics. Further studies of these so-called anomalous cells are to be made with a more rapidly moving galvanometer.

Theoretical Discussion.

More extended experimental data must be at hand before a theoretical discussion becomes profitable. It will be remembered however that Pfund[2] found the sensibility maximum of selenium to lie in the region of increasing transparency. Nicholson's[3] experiments also have a bearing in this connection. Koenigsberger[4] and Mueller[5] have found for stibnite an increasing transparency at the edge of the visible spectrum and Trowbridge[6] found a temperature shift of the transparency maximum of molybdenite of about the same magnitude as was found in these experiments for the sensibility maximum. While the evidence is far from conclusive, one is naturally led to look for some connection between the electrical and optical properties in selenium and stibnite. Bearing this in mind, it is to be remembered that only investigations of the optical and electrical properties which are carried out on the same sample, are comparable. If it should happen that a parallelism exists between the optical and electrical properties of these two substances,

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[1] Phys. Rev., Vol. 1, series II, p. 237; Phys. Rev., Vol. 1, serles II, p, 245.

[2] Pfund, Phys. Rev., XXVIII., No. 5, 1909.

[3] Nicholson, Phys. Rev., Vol. III., No. 1, 1914.

[4] Koenigsberger, Ann. d. Phys., Band 43, heft 8, p. 1205, 1914.

[5] Mueller, N. J. F. Min. Blbd. 17, 244, 1903.

[6] Trowbridge, Phys. Rev., Vol. II., No. 5, Nov., 1905.

then there can be no doubt that the mechanisms of absorption and increased conductivity are intimately connected.

SUMMARY.

To summarize the results of this paper:

1. A new form of selenium cell has been prepared particularly adapted for low temperature work.

2. Sensibility curves of selenium and stibnite at 20° C. and – 190° C. show that lowering the temperature causes: (*a*) A shift of the sensibility maximum towards the region of shorter wave-lengths by about 600 A.U. for both stibnite and selenium; (*b*) An extension of range of sensibility from 0.9 μ to at least 2 μ for both selenium and stibnite.

3. Sensibility curves for the same stibnite cell for both equilibrium exposures and exposures of ten seconds show a shift towards longer wave-lengths for the equilibrium exposures.

4. Investigation of the law connecting deflections and energy shows: (*a*) For equilibrium exposures, both stibnite and selenium obey the square root law, *i. e.*, $D = KE^{\beta}$ where-$\beta = 0.5$ approximately. (*b*) For stibnite at – 190° C., exposure ten seconds, $\beta = 0.77$.

5. Both selenium and stibnite show voltage effects.

6. These results seem to indicate that the mechanism which brings about light sensitiveness in selenium and stibnite is of the same general character.

In conclusion I wish to thank Professor J. S. Ames for suggesting the problem and for his interest throughout the investigation. To Professor A. H. Pfund for his many helpful suggestions and his constant encouragement I wish to express my sincere appreciation.

JOHNS HOPKINS UNIVERSITY,
May, 1914.