THE ACTION OF MERCURY VAPOR ON SELENIUM.

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PREVIOUSLY[1] I have shown that all the known changes of conductivity of selenium with the time of exposure to light can be explained mathematically by assuming a dynamic equilibrium between three components A, B and C. But in this analysis there appeared on obvious physical interpretation of the varying initial rates of change which were imposed on the different varieties of selenium for equilibrium in the dark. This fact has led the author to search for the conditions which will consistently and certainly produce one of the varieties of selenium about which there is most dispute, viz., light-negative selenium. The question as to whether the light-negative property is in the selenium itself or is in impurities, or selenium compounds, was one that had to be definitely settled. While the search has not answered all questions that have arisen, it has proved worth while in that it has resulted in some definite advances, that are interesting and which further limit future investigations. It is found that mercury vapor will uniformly transform different allotropic modifications of selenium into light-negative selenium, and further that the mercury vapor probably forms chemical union with the selenium.

In considering a relationship which I observed between the conductivity of selenium and its sensibility, viz., that light-negative selenium is associated with high conductivity, it occurred to me that any method that produces low resistance selenium might also at the same time produce light-negative selenium. In this connection it was noted that Moss[2] and later Minchin[3] had observed the remarkable decrease of resistance of selenium when it was placed in a vacuum produced by a mercury pump. Moss first exposed a bar of vitreous selenium to mercury vapor in a partial vacuum, whereupon he observed that the conductivity increased to a higher value than that of any known modification of selenium. He attributed this conductivity to a mercury film, and consequently it is not surprising that he overlooked the negative action of light. Minchin placed a light-positive selenium cell in a Sprengel vacuum. He observed that cells of several hundred thousand ohms decreased in resistance in

[1] PHYS. REV., 33, pp. 1 and 403.

[2] Phil. Mag., Ser. 5, 3, p. 67, 1877.

[3] Nature, 77, p. 198 and p. 222, 1908.

three or four days to values as low as 50 ohms, but he did not observe any light sensitiveness after the low resistance was reached.

THE CRYSTALLIZATION OF SELENIUM IN AN ATMOSPHERE IN WHICH MERCURY VAPOR IS PRESENT.

The first experiments that exhibited the action of mercury vapor on selenium were those in which the selenium in an ordinary cell form was crystallized in the presence of mercury vapor in air. The cell form consisted of two parallel wires wound around a porcelain cleat such as is used by the electrician for holding and insulating wires. The selenium was first melted on this cleat and then undercooled, thus giving the vitreous allotrope attached to the wires. This selenium form was then placed just over a heating bath of quartz sand. At the bottom of the sand was a globule of mercury. The bath was heated by a bunsen burner from below, and consequently the temperature of the mercury was much higher than that of the selenium. It was found that if the selenium was kept anywhere between 150° and 200°, its conductivity reached a very high value, which it maintained after cooling to room temperature. Immediately upon cooling the selenium displayed light-negative characteristics, *i. e.*, the conductivity decreased when the cell was illuminated.

It seems that the mercury diffused up through the sand and condensed on the selenium. As might be expected the higher the temperature of the sand bath and of the selenium, the sooner did the selenium reach an approximately constant high conductivity. If the selenium were kept at about 190° for about 10 minutes, the resistance of the cell would drop to about 20 ohms, while if the temperature were kept at 150° several hours were required in order that this conductivity might be attained. No differences in the light-characteristics could be detected by varying the temperatures within the range noted. However if the selenium were heated below 140° or above 200°, the light sensitiveness did not appear. Perhaps at the lower temperature an appreciable amount of the mercury vapor did not reach the selenium while at the higher temperatures an explanation must probably involve chemical union of the selenium and mercury or special allotropic modification of the selenium. Some thirty samples were made in this way, with but the use of a single drop of mercury in the sand bath.

The characteristics of the light-negative selenium prepared in this manner were not investigated fully, but many of them behaved much like the specimen described by Miss Crum.[1] Aside from the light-

[1] PHYS. REV., 33, 538, 1911.

negative character, the irregularities and the lack of permanency were the most striking peculiarities. Frequently the resistance would take sudden jumps, particularly if the specimen was illuminated or jarred. Occasionally the selenium would be light-negative with faint illumination but light-positive with intense illumination, and even more frequently a specimen would temporarily change over from light-negative to light-positive character. At one time as many as one fourth of the samples in my possession were light-positive when tested with light of uniform intensity. Frequently the sensibility was quite great. One sample changed from 74.6 ohms in the dark to 104.0 ohms in the light. It maintained an average sensibility half as large for about a week. The irregularity of one sample is illustrated by the following readings taken with the selenium alternately in the dark and in the light, at intervals of about two minutes.

Resistance in Dark.	Resistance in Light.
100	117
100	101.5
98.8	105.0
95	

Not all the samples made in this way were permanent. The maximum change of resistance by light was probably greatest about two days after manufacture. After that time the sensibility gradually decreased until finally after a month there was almost no effect due to light action.

It was considered possible so far as the above experiment decides that the mercury vapor may have acted in any one of three ways. The mercury may have acted chemically on the selenium so as to form a selenide, it may have acted catalytically in a way to alter the equilibrium of the selenium components, or it may have been merely entrapped in the selenium, without otherwise essentially altering its electrical properties.

One basis for the belief in the formation of a selenide at this stage of the experimenting lay in the statement, in Watt's Dictionary of Chemistry, that mercuric selenide is formed when mercury and selenium are heated together. However I noted that mercury did not freely combine with selenium, even when the latter was heated to its melting point.

If the mercury were trapped in the selenium by some absorption process so as to form a kind of solid solution, we would at once have an explanation of the high conductivity that always accompanies this light-negative property. Perhaps the light action merely alters the form of the crystals in all varieties of selenium similarly, and in this light-negative variety it thereby breaks the conducting film of mercury. This is a simple and apparently satisfactory explanation. It readily accounts for the irreg-

ularity and non-uniform behavior of the new selenium form. However it does not explain why light-negative selenium should be produced in the presence of mercury vapor, under conditions that would not produce any light sensibility at all in the absence of mercury vapor.

Should the mercury vapor act catalytically, so as to alter the rates of change of the existent components in the selenium, we have at once a satisfactory explanation. The first difficulty in the way of this explanation is the possible formation of a selenide. More will be said later concerning these theories.

THE EFFECT OF UNHEATED MERCURY VAPOR ON LIGHT-POSITIVE SELENIUM.

There was considerable uncertainty in the last experiment as to whether the mercury vapor at the high temperature may not have acted on selenium by chemical union. If such chemical action did not take place then it seemed reasonable to hope that mercury vapor at room temperatures might transform light-positive selenium into light-negative selenium. This is particularly consistent with the view that in the light-negative selenium the conducting material is essentially mercury, which is broken and altered by the selenium crystals changing form under the action of light.

Accordingly two small cells, made by dividing a regular size Giltay cell into parts, were placed in an apparatus connecting with a Gaede vacuum pump. The resistance of each sample was upwards of twenty million ohms, in the dark, and possessed the usual sensibility to light. After being kept in a vacuum of less than .01 mm. for twenty minutes there was no apparent change in resistance, but after being in the vacuum for twelve hours the resistance had fallen to 40 ohms. At first the irregularity of behavior when illuminated resembled that of the light-negative samples previously described. The resistance was so unsteady that it was difficult to say just what action was due to the light. The cell was then placed in a kerosene bath. After resting thus for several hours, it showed consistent light-negative properties. The following is a sample of the observations taken with the selenium alternately in the dark and illuminated with a 16 c.p. lamp at 20 cm. distance.

Resistance in Dark.	Resistance in Light.
70.5	70.6
70.5	70.61
70.5	70.58
70.5	70.56
71.3	71.5

And after resting three months in the dark, the behavior is illustrated by these readings. The illumination was approximately that above.

Resistance in Dark.	Resistance in Light.
86.3	86.43
86.33	86.43
86.33	86.50
86.0	86.12
86.0	86.11

The curve in Fig. 1 shows the manner in which the resistance changes with the time of exposure. The rate of change is not nearly so rapid as that of a light-negative sample for which the curve is given in Fig. 9 of a former paper on the "Nature of Light-action in Selenium."[1]

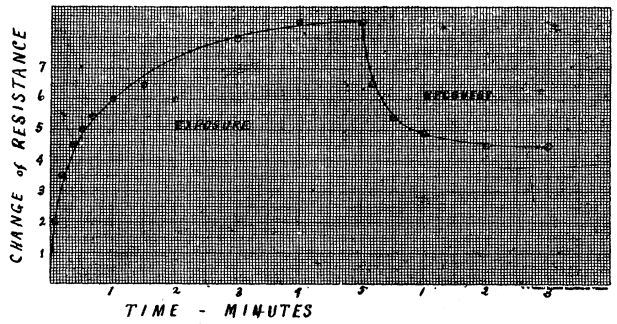

Fig. 1.

The difference in these two may be accounted for by the unequal light intensity in the two instances. At any rate the resistance begins to decrease at the instant of illumination in these new samples, and the change is so rapid at first that it is quite improbable that it is due to heat rather than light action. To definitely determine this point I hope soon to be able to map the sensibility of this variety of selenium throughout the spectrum, as Pfund[2] has done for light-positive selenium. Such a determination may also aid in a physical interpretation of the nature of the change of resistance.

The second sample referred to above was weighed before and after exposing it to the mercury vapor, to detect if possible the amount of mercury that was necessary to perform the observed transformation. Before placing in a vacuum and while the resistance was several million ohms the weight was 1.2527 gm. After exposing to mercury vapor in a partial vacuum for 16 hours, the resistance fell to 104 ohms. The

[1] PHYS. REV., 33, p. 19.

[2] PHYS. REV., 34, p. 370, 1912.

weight had not changed by as much as 0.1 milligram. This result is not inconsistent with the supposition that the increase of conductivity arises solely from the direct conductance of the absorbed mercury vapor. For if it is assumed that the mercury vapor has the same conducting power as large masses of mercury, it can be readily calculated that a film of mercury 2.5×10^{-9} cm. thick would have been sufficient to account for the observed conductivity. Further the weight of such a film would be only 1.2×10^{-8} gm., which amount it would be impossible to detect by weighing. But even with this small amount of mercury inside the selenium the concentration of mercury would be about a billion times as dense as that in a saturated free space at the same temperature.

THE ACTION ON POWDERED RED AMORPHOUS SELENIUM.

If in the Giltay cell, we could have been certain that all the selenium was acted upon, we would have known by the absence of increased weight that no chemical action took place. But as there was no obvious change of color or appearance, no estimate could be made of the extent of action of the mercury vapor.

The red amorphous selenium was exposed to the mercury vapor in a vacuum with the hope that a change in color would indicate the extent of the action. First a very small fraction of a gram of the red powder was scattered in the vacuum tube. Within half an hour after high vacuum was reached this selenium had turned black. The selenium was then packed between two wire electrodes. The resistance was fairly steady at 240 ohms. It was also light-negative, showing an increase of from 0.5 to 20 ohms. After heating for thirty minutes at 210° the resistance was reduced to 1.2 ohms. For a week following this heating the resistance was unsteady and slowly increased in value. However it did become steady after this interval and it was then quite light-sensitive. Several light-negative samples were made by packing this black selenium between wire electrodes. They were all of very low resistance and light-negative in character.

The fact that the red amorphous form did change its color to a distinct black, made it seem apparent that chemical action did not take place. If mercury selenide were formed, then when all the selenium changed to the black form it should increase in weight by the ratio of 79 to 200.

TWO SAMPLES OF RED SELENIUM WERE WEIGHED AS FOLLOWS:

Test No. 1.

Weight of glass tube container	1.066 gm.
Container + selenium	1.661
In vacuum 4 hours, 90 per cent. black	1.674
In vacuum 12 hours	1.667
In vacuum 10 hours longer	1.660

Test No. 2.

Weight of paper	0.514 gm.	
Paper + red amorphous selenium.	.808	
After 4 hours exposure to vapor	.803	
After 12 hours longer exposure	.803	
Exposure continued 6 hours	.808	selenium almost entirely black.
Exposure continued 4 hours	.797	mercury heated slightly.
Exposed to air 16 hours	.815	
Exposed 10 hours longer in vacuum	.801	
Exposed to air 3 hours	.813	

A third test was made using 2.013 grams of selenium. After exposure for about 60 hours the selenium was mostly blackened, and the weight had increased to only 2.033 grams. During exposure the effect of the mercury vapor did not penetrate far into the mass of powder. It was seldom blackened deeper than a millimeter, so that it was necessary to frequently stir a fresh surface for exposure. The second test showed what seemed to be the hygroscopic property of the selenium, by an increase in weight when it was exposed to the air. The fact that the selenium is blackened only near the surface, leads to the belief that the absorbed moisture does not play a very important part in the transformation.

The figures in these three tests apparently demonstrate that chemical combination between the selenium and the mercury vapor is quite inconceivable. If there were any definite measurable increase of weight due to the absorption of mercury vapor, it is masked by the variations in weight due to moisture and uncertain causes.

However I was deceived here by assuming that because the selenium was blackened in from 4 to 60 hours, and increased in weight by less than .03 gram that there could be no further action between the mercury and the selenium. The truth is that while it was blackened it was not all acted upon. After being exposed 1,230 hours in a high vacuum a sample weighing 0.565 gram increased in weight to 1.803 grams. When the vacuum was kept at the X-ray stage the increase was almost uniformly one milligram per hour for the first 1,000 hours, but during the next 200 hours, the weight increased more and more slowly. If mercuric selenide were formed the weight should have ultimately increased to 1.995 grams. The fact that this weight was not quite reached can easily be explained by the loss of selenium during weighings and by diffusion of its vapor in high vacuum, if not to the fact that sufficient time was not allowed for complete penetration and action.

I do not believe it right to assume at this time that the mercury vapor in a finely divided state in the selenium can have these light-negative

properties, except for the action of light on selenium or the selenium compound.

One determination of the density of this new selenium gave 4.98, but this particular sample may have had some free mercury with it. With my arrangements it is a slow process to produce a sufficiently large quantity for an accurate determination of the density. A globule of mercury acts very rapidly on selenium surrounding it in a vacuum but at atmospheric pressure a mercury globule in contact with the red powder will not perceptibly color the selenium in several days. Later I hope to obtain the density more accurately. It will probably show the same density as mercuric selenide, which in fact it resembles.

It may be mentioned that powdered vitreous selenium when placed in an atmosphere of mercury vapor for 18 hours also assumes a high conductivity and the light-negative property. There is no apparent change in the color of this modification. It is rather strange that any powder should have such a high conductivity when rather loosely packed as the powders here were packed. The interaction between the mercury and the selenium arises probably more essentially from a property of the selenium. Powdered sulphur when exposed several days to mercury vapor at the same time the selenium was exposed showed no conductivity at all.

SUMMARY.

1. Mercury vapor acts on selenium in such a manner as to produce a very high conductivity and the light-negative property.

2. The mercury acts on the amorphous form and probably also on the other modifications so as to produce selenium of new characteristics. Permanent chemical compounds are probably formed between the mercury and the selenium.

3. A very easy and satisfactory method of making light-negative selenium cells is to place the amorphous selenium in a mercury vacuum until it becomes black, and then to press this black selenium between fixed electrodes.

4. The energy curve should be mapped out in order to gain evidence as to the similarity of action of light in this and light-positive selenium.

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