

THE EFFECTS OF GASES AND METALLIC VAPORS ON THE  
ELECTRICAL PROPERTIES EXHIBITED BY SELENIUM  
CRYSTALS OF THE HEXAGONAL SYSTEM.

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THE photo-electric effect of certain crystals and metals has been observed to vary with the freshness of their surfaces, and with the different kinds of gas surrounding them.<sup>1</sup> It has also been suggested that perhaps the well-known action of light on selenium might also vary with the surface conditions, even though it is generally accepted that the change in selenium due to light is a volume, and not a surface effect.<sup>2</sup>

The following experiments were undertaken to ascertain what effect, if any, various vapors or gases would have on crystals of selenium. It was necessary to make crystals all under exactly similar conditions as to pressure, temperature, and rate of cooling upon removal from the incubator, in order to establish their uniformity. A set of eight tubes of selenium was evacuated at one time; sealed off separately, and placed in a Frease oven regulated for 185° C. Before sealing off the tubes, and while they were being evacuated, the selenium was boiled for about fifteen minutes to drive off all the gases in the stick selenium. The crystals were formed in sixty-nine days.

Of these eight tubes, three were picked at random for test crystals. The others were filled with the different gases and put aside that the crystals might soak in the various gases and come to a saturation point. The gases used were hydrogen, argon, nitrogen, oxygen and air. Air was taken as a standard for comparison. The vapors used were mercury, tin, bismuth, sulphur and arsenic.

## THE EFFECT OF GAS ON SELENIUM CRYSTALS.

Before attempting to ascertain whether the gas in which the different crystals had soaked produced any change in their electrical properties, *i. e.*, their resistance, sensitiveness to light, maximum wave-length sensibility, rate of action under light, and rate of decrease of resistance upon removal of light stimulus, it was necessary to determine whether

<sup>1</sup> T. Wulf, Ann. der Physik, 9, pp. 946-963, 1902. Kunz and Stebbins, Phys. Rev., Vol. 7, p. 62, 1916.

<sup>2</sup> F. C. Brown and L. P. Seig, Phil. Mag., Vol. 28, p. 497, 1914.

crystals made under similar conditions acted alike when subjected to similar treatment after production.

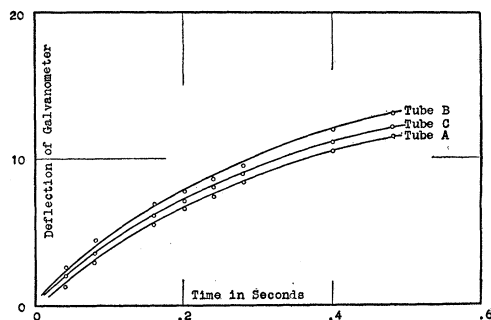


Fig. 1a.

For this point, crystals from various parts of each of the three test-tubes were selected, and their properties determined. The crystals chosen were taken as near the same size as was possible to select them without microscopic measurements. The mean specific resistance for the test crystals was found to be  $8.5 \times 10^5$  ohms per sq. mm. In Fig. 1

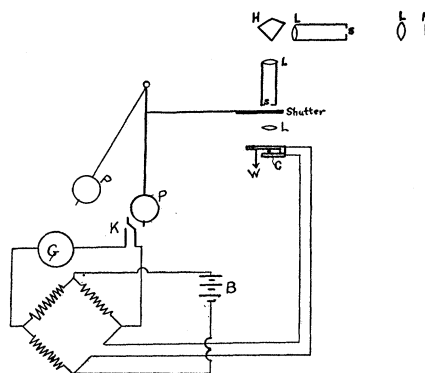


Fig. 1.

Action curve of test crystals.

is shown the action curves for these crystals. They were obtained by placing the crystals in the contacts shown at C in the diagram of apparatus, where the crystal was in the dark, and then subjected to the action of light for intervals varying from .04 second to .48 second, and measuring the resultant change in resistance. The change from equilibrium in the dark to that in the light was then plotted as a function of the time. It is seen that in general the slope of the curves are the same, indicating that the rate of decrease of resistance with time under given light condi-

tions is constant. For the recovery to normal dark conditions after being exposed to the light, a constant  $\alpha$  was calculated from the theory of recovery proposed by Dr. F. C. Brown.<sup>1</sup>

This theory assumes a certain similarity between the theory for recombination of negative and positive electrons in gases and the recombinations of negative electrons and positive residues in selenium crystals. Rutherford<sup>2</sup> has shown that if in a gas  $n_1$  negative and  $n_2$  positive ions are present, the rate of recombination is directly proportional to  $n_1 \times n_2$  expressed by the equation:

$$\frac{dN}{dt} = -\alpha(N_1 \times N_2),$$

where  $\alpha$  is a constant called the coefficient of recombination. It assumes that for short intervals of time after the light has been cut off that the decrease in conductivity of a selenium crystal is due to the recombination of the conducting electrons with the positive residues, and that this recombination takes place according to the same law as that which holds for gases. If the number of electrons taking part in the conduction is proportional to the conductivity, the rate of recombination may be calculated from the equation:

$$\alpha = -\frac{dC}{C^2 dt},$$

where  $dC$  is the decrease in the conductivity during the time  $dt$  that the crystals have been in the dark;  $C$  is the equilibrium value of the conductivity in the light; and  $\alpha$  is proportional to the coefficient of recombination. It is therefore necessary to assume:

1. When a crystal is in equilibrium in the light or in the dark the conductivity is proportional to the number of negative electrons taking part in the conduction.
2. Recombination takes place in selenium crystals according to the same law as in gases.
3. The rate of recombination in the light is the same as in the dark.

The constant  $\alpha$  was measured for crystals from the tubes of test crystals, and were found to be for

tube A.....	$2.68 \times 10^5,$
tube B.....	$2.90 \times 10^5,$
tube C.....	$2.84 \times 10^5.$

These values are in very good agreement.

<sup>1</sup> PHYS. REV., Series 2, Vol. 5, p. 395, 1915.

<sup>2</sup> Phil. Mag., Ser. 5, vol. 44, p. 422, 1897, and Ser. 5, vol. 47, p. 109, 1899.

In Fig. 2 is shown a further similar relation between these crystals from the tubes of test crystals. These curves are a relation between

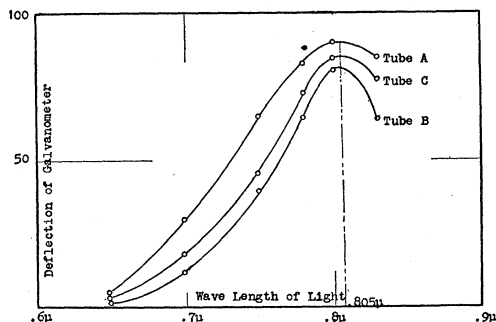


Fig. 2.

Wave-length sensibility curves of test crystals.

resistance and wave-length of incident light, and show what is known as wave-length sensibility relations.

They were obtained by placing the various crystals in the same position *C* in the apparatus diagram and subjecting them to the same spectrum, produced by a Hilger monochromatic illuminator, where this spectrum was not an equal energy spectrum for all wave-lengths, but was the same energy for all crystals at any given wave-length. The curves are of the same shape and show uniformly a maximum wave-length sensibility at a little further in the red end of the spectrum than  $.8 \mu$ —roughly about  $.805 \mu$ .

From the various tests here applied, it is justifiable to assume that the crystals in the entire set of tubes made at the same time under identical conditions of pressure, temperature, and rate of cooling, would show identical properties of resistance, light action, recovery from light, and wave-length sensibility if they were all treated alike after production. And further, that if any difference be detected after subjecting them to different treatment, that this treatment is the cause of the difference found. These crystals will therefore be assumed to be normal crystals made in vacuum and tested in air, and the various other crystals will be compared to them. The results will not be referred to absolute measurements, but will be entirely positive. Only one crystal from each tube will be used in the comparisons, but each one has been checked against many others selected at random from the same tube to be certain that it is not an isolated crystal.

In Fig. 3 is shown the action curves for the different crystals. They were obtained as were the corresponding curves for the test crystals,

but show a marked variation from the similarity noticed there. It will be observed that the crystals treated with nitrogen show a decidedly greater slope than any of the others, and the fact of a more rapid rate of

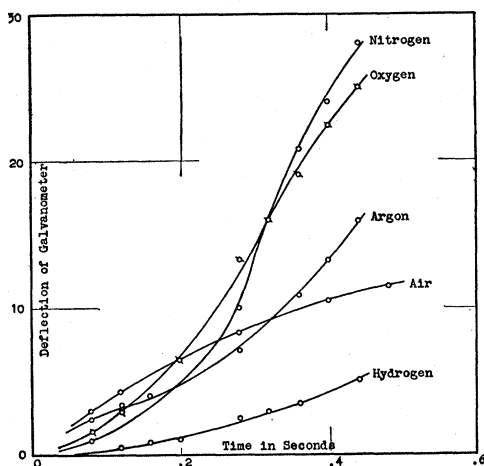


Fig. 3.  
Action curves.

change of resistance with light stimulus, as these curves indicate, is very noticeable in working with the crystals. The hydrogen-treated crystals are the most sluggish over long periods of exposure, as well as for the short periods indicated in the curves. The air crystal is almost identical with those used as a standard.

Fig. 4 gives the rate of recovery data from which the coefficients of

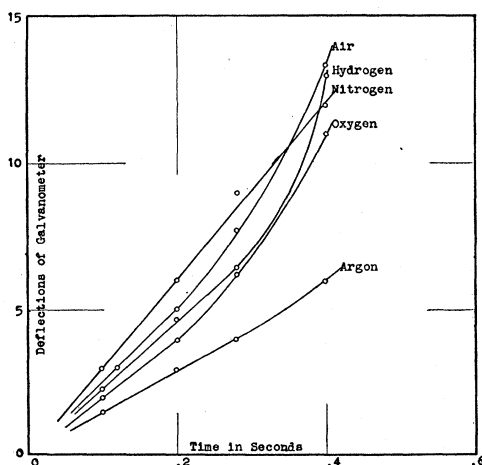


Fig. 4.  
Recovery Curves.

recovery were computed. For short intervals of time the nitrogen-treated crystals again show a more marked rate of change than do the others. Argon crystals are very slow in their recovery after exposure to light.

The wave-length sensibility curves in Fig. 5 are particularly interesting. It is to be noticed that nitrogen crystals have changed at their maximum about fifty per cent. more than the comparison crystals changed. In

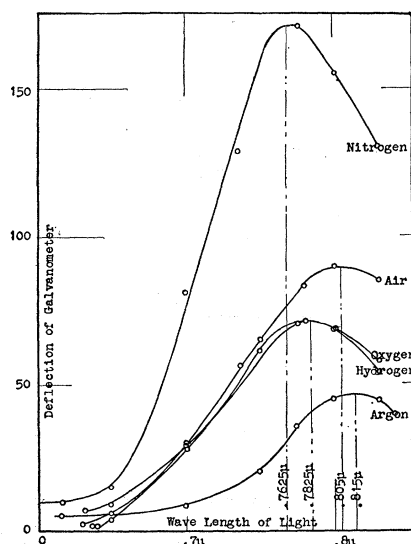


Fig. 5.

Wave-length sensibility curves.

white light, the nitrogen crystals changed their resistance so that the ratio of resistance in the light to that in the dark was 3.4, while the ratio for the comparison crystals was 3.2. Oxygen ratio was 2.8, hydrogen 3, and argon 2.5. These curves show that in monochromatic light the ratio of resistance change is of the same order—nitrogen showing the largest ratio, and the argon crystals the smallest.

These curves also show a decided difference in the wave-length at which the various crystals reach a maximum. The observations show decided maxima at the wave-lengths indicated. There seems to

be no reason why these different maxima should show the law of progressive variation with the gases that the resistance and other effects show.

TABLE I.

	Wave-length Sensibility. (From Fig. 5)	$\alpha$	$R_d \div R_L$	Specific Resistance.	Atomic Weight.
N.....	1	$10.3 \times 10^5$	3.4	$1.16 \times 10^5$	14
Air.....	2	$2.68 \times 10^5$	3.2	$8.5 \times 10^5$	
O.....	3	$1.7 \times 10^5$	2.8	$7.5 \times 10^5$	16
H.....	4	$1.37 \times 10^5$	3	$14.5 \times 10^5$	1
Ar.....	5	$1.07 \times 10^5$	2.5	$9.2 \times 10^5$	40

In Table I. is recapitulated the various facts observed. In the first column the crystals are arranged according to their amount of change in resistance at their maximum wave-length sensibility, as shown in Fig.

5. In the second column, values of  $\alpha$  are shown, and in the third, the factor showing the ratio of their resistance in the light to that in the dark is given. The fourth column shows the specific resistance of the various crystals, but is subject to considerable error due to the smallness of the area of contact. It is to be noticed that the crystals showing the greatest change in resistance from light to dark also show the greatest coefficient of recombination, as indicated by  $\alpha$ . They also show the greatest change at their most sensitive wave-length, and in general, the least specific resistance.

It seems that of these gases, nitrogen improves the action of the crystals far more than do any of the other gases, and that argon does the most damage. Now from the work of Kunz and Stebbins<sup>1</sup> and others, who have shown that argon is one of the most effective gases in photo-electric effects, it seems correct to conclude that there is no relation between photo-electric effects and light sensitiveness in selenium, as is shown also by F. C. Brown in some recent unpublished results.

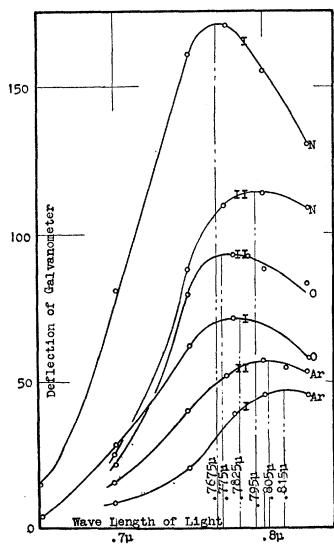


Fig. 6.

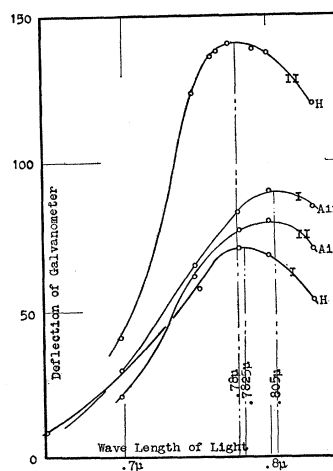


Fig. 7.

Wave-length sensibility curves of crystals taken from vacuum to gas to air.

Inasmuch as nitrogen appears to be the most helpful of these gases the other gases seem also to be arranged in order naturally, because air containing four fifths nitrogen, about one fifth oxygen, and small parts of hydrogen and argon, should be next to nitrogen, and should be better than the others, as is shown to be the case. Also, oxygen should come

<sup>1</sup> PHYS. REV., p. 62, Vol. VII., 1916.

third, as it does. Hydrogen and argon follow in their order. Now arranged according to atomic weights, except for hydrogen, these gases also occur in order—the heavier gas being more detrimental than the lighter ones. Hydrogen may be peculiar in its action here as it is in its action on platinum.

After the various tests before given were made, the crystals were placed in separate glass containers, and allowed to stand in dry air ninety days, when they were again tested for maximum wave-length sensibility, and for the values of  $\alpha$ . In Figs. 6 and 7 these last curves are compared with those shown in Fig. 5. The curves of Fig. 5 are marked *I* and those of the last tests are marked *II*, and are presented to show the different degrees of change in the differently treated crystals. It will be noticed that the crystal taken from the vacuum tube to air (Fig. 7), has changed but very little, either in sensitiveness or wave-length at which a maximum occurs. The hydrogen crystal has changed more than other—its change in conductivity is about 100 per cent., and its maximum now occurs at  $.7825\mu$  instead of  $.78$  as formerly. The conductivity of the nitrogen crystal has been reduced by a factor of two thirds, and its maximum shifted from  $.7675\mu$  out to  $.795\mu$ . The oxygen and argon crystals have changed, as can be observed, but in less degree. The principal point for these two is the shift of the maximum (Fig. 6). The values of  $\alpha$  shown in Table II. are of interest. These show, as do the curves in

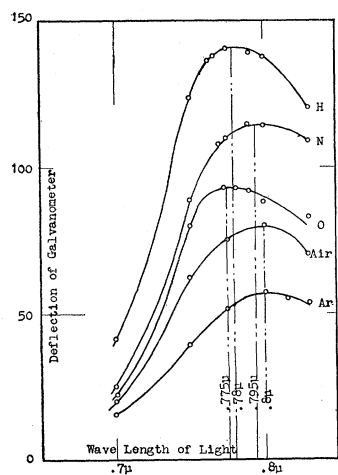


Fig. 8.

Wave-length sensibility curves.

TABLE II.

	After Soaking in Gas.	Ninety Days Later in Air.
N.....	$10.3 \times 10^5$	$3.05 \times 10^5$
Air.....	$2.68 \times 10^5$	$2.62 \times 10^5$
O.....	$1.7 \times 10^5$	$2.64 \times 10^5$
H.....	$1.37 \times 10^5$	$1.65 \times 10^5$
Ar.....	$1.07 \times 10^5$	$5.18 \times 10^5$

Fig. 8, a tendency towards the value of the crystals observed in air throughout the experiment. The recovery of argon has increased by nearly five times, and oxygen two times. Nitrogen has decreased to one third its former value, and air and hydrogen have remained nearly as before. In Fig. 8 the curves marked *II* in Figs. 6

and 7 are compared with each other to show the contrast with the same crystals shown in Fig. 5.



## CRYSTALS MADE IN NITROGEN AND HYDROGEN.

At the same time that these previous crystals were made in vacuum tubes, selenium was crystallized in an atmosphere of nitrogen, and also of hydrogen. The results were different than for those made in vacuum and soaked in these gases, the reason being that the gas in the tube was at a pressure of nearly two atmospheres, which altered the temperature gradient as well as modifying the pressure under which the crystals formed. The maximum wave-length sensibility for crystals made in hydrogen was the same as for crystals made in vacuum and soaked in hydrogen—both occurring at approximately wave-length  $.785 \mu$ . There were no remarkable properties of these crystals except that they were very slow of action, as were also those made in vacuum and soaked in hydrogen, requiring at least ten minutes to reach an approximate equilibrium value from dark to light, and requiring hours to recover approximate equilibrium from dark to light.

The crystals made in nitrogen furnished more interesting results. At times they would respond as do the normal crystals, that is, those that in response to light decrease their resistance by certain ratios, depending upon the time of exposure and the intensity of the light. At other times these same crystals would suddenly decrease their resistance while remaining in the dark, and upon exposure to light in this condition, would increase their resistance. There seemed to be no good explanation of these effects, but it had been previously observed that during the process of baking the crystals there had developed in this tube a small crack. The probability of effect by gases was dismissed, but the possibility of the entrance of metallic vapor from the heating coils of the oven suggested a series of experiments to determine their effect on selenium crystals.

## THE EFFECT OF METALLIC VAPORS ON SELENIUM CRYSTALS.

A tube of selenium was prepared as previously described for making crystals, except a small tube filled with fillings of pure tin was put in the larger tube along with the selenium. There was no contact between the selenium and the tin except in the vapor state, both being at a temperature above the melting point of tin. Crystals formed without any visible difference in color, size or general appearance. Their resistance was of the same order of magnitude as for those prepared in the usual manner—about  $2$  to  $3 \times 10^5$  ohms per millimeter cube. However, they were strikingly different from normal in that they were absolutely neutral to the action of light within the limits of the galvanometer which had a sensitiveness of  $10^{-9}$  amperes. A 500-watt nitrogen-filled lamp at a

distance of 50 centimeters had no effect on the conductivity of any of these crystals.

When sulphur replaced the tin in the small inner tube, the crystals were exceedingly irregular, and very short and thick. In general they were decidedly grayish in color. Their resistance was several times as much as normal crystals, and their resistance change with light was of the same order as these vacuum-made crystals. Their maximum sensibility occurred at  $.83 \mu$ , with very sluggish recovery and action rates. The remarkable fact about the experiment with sulphur was the number of red crystals produced. These red crystals were exceedingly small—too small for definite analysis—but when viewed through a microscope their angles could be definitely seen. When viewed through crossed Nichols they appeared a brilliant red, indicating a double refracting power—a character purely crystalline. When tested for conductivity, to the limits of the apparatus, they showed none. Red crystals of selenium produced by sublimation are particularly rare, having been, so far as known, obtained but once, and those by F. C. Brown.<sup>1</sup>

When bismuth replaced tin, there was no apparent deviation from the normal crystals.

Normal crystals made in vacuum and tested in air were placed in metallic vapors, and their resistance changes observed. The crystals were arranged so that they were not heated as the vapors were drawn over them by means of a pump. All the metallic vapors showed the same effects. If the vapor was drawn over them for too long a period, a thick coating deposited, and there was no other change in the crystal's apparent resistance than a decided lowering, due entirely to the conducting film of metal, and there was no light sensitiveness. If, however, a sufficiently thin layer were deposited by varying the time of exposure to the vapor, for small currents, the resistance would be very low—as for example a crystal whose dark resistance was  $3.9 \times 10^6$  ohms, when placed in tin vapor for four hours, showed a resistance of  $9.9 \times 10^3$  ohms. In its original state the crystal was light positive, but in the second state it was light negative. Its negative action was not steady, however. This result was typical of the action of the vapors of bismuth, arsenic and mercury.<sup>2</sup>

There is a possible explanation of this action. It is well known<sup>3</sup> that if a small V-shaped trough has a fine thread of mercury in the bottom, and a current be sent along it, there is a tendency for the mercury to form globules, which breaks the current. This tendency depends upon

<sup>1</sup> *PHYS. REV.*, N. S., Vol. IV., No. 2, Aug., 1914, p. 85.

<sup>2</sup> F. C. Brown, *PHYS. REV.*, N. S., Vol. II., No. 2, p. 153, Aug., 1918.

<sup>3</sup> E. F. Northrup, *Metallurgical and Chem. Eng.*, Jan., 1913.

the size of the current and the size of the thread of mercury. Now with a very thin layer of the metal on the crystal, a small current which is shared by both the crystal and the thin layer will not cause the layer to ball up, but upon subjecting the combination to light, there is enough additional current permitted to flow by the action of the selenium to cause the layer to ball up and break the circuit through it, thus causing all the current to go through the crystal. This, in turn, due to the high resistance of the crystal, causes an apparent light-negative action, *i. e.*, an increase of resistance due to light, instead of the normal decrease. Such a continuous action would cause such fluctuations of the currents as are observed. If one of these crystals showing varying resistance features due to a layer of condensed metallic vapor be connected in the apparatus shown in the diagram of apparatus, and an electro-magnetic wave be sent through the room by the spark from an induction coil, the resistance will instantly increase to approximately its normal value, and for a particular one tested, it required ninety-six hours to again reach a low resistance, having remained undisturbed meanwhile. The action of the electro-magnetic wave is to send a very appreciable current through the layer (the circuit acting as an antenna), which breaks up the film to a larger extent than can occur under the action of light.

#### SUMMARY.

1. It has been shown that selenium crystals of the hexagonal system show identical properties when they have been subjected to the same conditions during and subsequent to their production.
2. That their various light electrical properties may be altered by subjecting them to the action of different gases. Whether these gases, in a gas layer, change crystal stresses, or vary the energy received from a constant source is not determined.
3. That the effect of the gas seems to be more detrimental the higher the atomic weight of the gas.
4. That the effect of making crystals in gases is but little different than making crystals in vacuum, and subjecting them to gas.
5. That the effect of metallic vapors is to form a conducting film on the surface that may, under certain conditions, give an apparent light-negative action to crystals that are normally light positive.