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PHYSICAL REVIEW.

THE PHYSICAL PROPERTIES OF SELENIUM.

By P. J. Nicholson.

EVER since the discovery of the sensitiveness of the electrical resistance of metallic selenium to alteration in illumination, attention has been given to the problem of finding an explanation for the phenomenon. In late years, two views have been expressed regarding this. Pfund[1] introduced the idea that the effect is due to a resonance of the electrons in the atom, occasioning explosions which lead to an increase in the number of conducting electrons. This view has found favor with some investigators, particularly with Ries to whom a great amount of valuable work is due. It deserves attention for various reasons: First, the ultimate explanation found must be in terms of the electron theory if that theory is to remain a permanent part of our physical science. Again, the idea of resonance is a very plausible one to explain such an increase of conductivity. The second theory may be construed as quite in harmony with the first. Marc and others have obtained evidence that there exist at least two forms of metallic selenium of widely different electrical resistivity; and it is assumed that illumination brings about a transformation from the less to the more conducting of the two. This theory has been amplified and put in mathematical form by Brown,[2] who assumes the existence of three forms, selenium *A*, *B* and *C*.

As tests of these views, several lines of work suggest themselves, and the object of the present series of experiments was to obtain data that would be of help in the solution of the problem. Since the ultimate explanation must take into account the physical characteristics of the element, one of the first requisites is that satisfactory methods be obtained for the production of good films of selenium in its various forms. Accordingly, the first part of the work had that end in view. In the second

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[1] Phys. Rev., XXVIII., 324, 1909.

[2] Phys. Rev., XXXII., 237, 252, 1911.

part, on the other hand, experiments having an immediate bearing on the theories to be tested were taken up.

SPUTTERING OF SELENIUM CATHODES.

There seems to be a great deal that is difficult to determine connected with the sputtering of selenium cathodes. Here, the observations of Longden[1] and later of Pfund,[2] that cathodes of metallic selenium do not yield films in the metallic form, was confirmed. When the current density is very small, films that are very thin but beautiful are yielded. Soon, however, the cathode becomes covered with a black powder which probably is some form of the element; and from that moment, satisfactory sputtering does not take place. Instead of continuous, semi-transparent films, layers appear that are wholly or in part granular in structure.

Since great difficulty has been experienced by different experimenters in obtaining semi-transparent films of metallic selenium by ordinary means, an effort was made to obtain them directly. The method that suggested itself at once was to keep the surface designed to receive the deposit at a temperature of 150° or thereabouts. This was done by using a small furnace of nicrome wire heated by a circuit that was taken through the base of the apparatus and insulated from it. For a variety of reasons, it was found very difficult to keep the pressure constant, and consequently, the temperature would vary. Nevertheless, several deposits were obtained whose surface possessed the appearance of metallic selenium; but their transmission, however, being reddish, showed the presence of some of the amorphous.

Accidentally, several films were obtained directly by sputtering from metallic cathodes which proved to contain at least a large fraction of the metallic form. One layer deposited on a platinum-on-mica grating was both conducting and light-sensitive. As its resistance was about 10^8 ohms, however, the cell was of little use. The conditions necessary for obtaining such deposits were not determined save that the cathode was always a metallic one that had been subjected to long heating near 200°, and that the current density was fairly great. It does not appear probable that this method will be of practical value in view of the ease with which good metallic layers can be obtained by the other process.

Films of amorphous selenium, on the other hand, can be formed by sputtering quite readily; but, if the current density is not very small, the cathode soon changes partly into the metallic state, and thereafter the films are granular, as before. It seemed desirable then to reduce the

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[1] American Journ. of Sci., X,, 55, 1900.

[2] PHYS. REV., XXVIII., 324, 1909.

heating effect within the apparatus to a minimum. With that end in view, a special cathode sputtering outfit was constructed. This will now be described.

Before the work had proceeded far, it was observed that alternating currents yielded quicker results than direct currents of equivalent voltage. This, no doubt, is due to the fact that the maximum voltage in the former is far in excess of the effective. It appeared better to use alternating current in all further work, but in order to decrease the heating effect, it should be rectified. This suggested the use of a point anode. The cathode was further cooled by a jacket of flowing water.

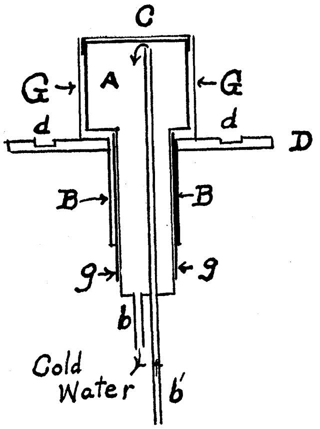

Fig. 1.

Section of cathode sputtering apparatus. *A*, brass chamber, fitted with brass tubes *b*, *b'* through which a steady stream of cold water was forced. *A* was fixed in brass tube *B* with cotinsky cement, and perfect insulation was assured by glass tube *g*. Top of chamber was made very thin and covered with a cap of aluminum foil *C*. Glass tube *G* kept discharge confined to top surface. Small bell-jar, fitted with point aluminum anode, was waxed into groove *d* in brass base, *D*. Wire frame supported plate receiving the discharge from 1 cm. to 3 cm. above *C*, while a piece of aluminum foil covered with a layer of selenium was placed on *C*, serving as cathode for the discharge.

All who have ever tried to secure films of selenium by cathode sputtering must have observed that often small portions of selenium fall on the plate receiving the film and become nuclei for beautiful concentric rings which soon form around them. In order to obtain uniform films, then, this effect had to be eliminated; and sputtering upwards[1] was the obvious remedy. The apparatus was found very satisfactory with work on selenium, and moreover, proved to be more satisfactory than the commoner form for obtaining films of other metals. For example,

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[1] This had been suggested by Dr. C. M. Sparrow for sputtering substances that cannot be made into continuous cathodes.

by its use, the time consumed in obtaining good mirrors of platinum was reduced by from one half to one third.

The vacuum found most advantageous was such that there was about one centimeter of dark space. As source of voltage a two thousand volt transformer was used. A large resistance was always used in series with the primary so that an E.M.F. of from a few hundred to two thousand volts was available. In no case could the latter be employed, for, as soon as its use was attempted, an emission of gas resulted that caused the pressure to rise above that which the work called for.

By means of this apparatus films of many kinds were obtainable. By using a fairly high current density, almost opaque films of amorphous selenium were deposited in less than one minute. It was found, however, that as a general rule, films deposited quickly were not as transformable as those deposited very slowly.

Other films were obtained that changed into semi-transparent metallic ones and stood long heating at a temperature near 200°. The pure metallic films were very easily distinguished by their plum-colored reflection and the absence of red in their transmission. Films with a good surface, but with some red in their transmission, are quite easily obtainable.

It was found that care should be taken to avoid having any sealing wax inside of the apparatus where the discharge might play on it. In addition to its emission of gas, this substance seems to have a special attraction for the selenium deposits, so that layers of the element accumulate on it in a very short time.

TRANSFORMATION OF THIN FILMS.

Considerable attention was paid to the transformation of selenium films, and this proved to be as enigmatical as the problem of sputtering. The question is here suggested whether transformation into the metallic state is ever complete or not. Some films, of considerable thickness, with beautiful red surfaces, withstood a temperature of 200° for twenty-four hours without showing any sign of transformation. Others would acquire a surface with the familiar plum-colored luster of the metallic selenium but whose transmission contained much red. Occasionally, a film was found which seemed to have transformed completely, having apparently no red transmission. These films were similar to that obtained by Pfund, whose optical constants were measured by him.

Some selenium films seem to vaporize quite readily. These could not be transformed satisfactorily, for it seemed that before transformation was complete, the continuity of the surface was destroyed. Others, again, changed into the metallic state quite readily, and these stood a heating up to nearly 200° for some hours. The conditions that must be fulfilled in order to transform thin films successfully seem to have partly to do with the process of heating and partly with the nature of the layer. One film on glass, about 2 inches square, was cut into small pieces, and each piece tried came over into the metallic state without difficulty provided the rate of heating was sufficiently slow. This indicates that the character of the films comes into play. All that can be said about the film is that it was yellowish in color, and was obtained when the rate of deposit was fairly slow while the glass plate was at a distance of nearly one inch from the cathode. All films so obtained, however, were not transformed, as the surface soon became broken, as mentioned above. It may be expected that if the pressure on the films were so increased as to cut down vaporization appreciably, transformation could be carried on successfully; and this is to be tested in a later experiment.

Ultra-Violet Absorption.

Several efforts were made to obtain a good semi-transparent film of selenium on quartz, with portions of two different thicknesses, so as to measure the optical constants in the ultra-violet. These, while untransformed, had absolutely no ultra-violet transmission. Although several films on quartz, of one thickness, were transformed, yet success was not met with in transforming films when portions were of different thicknesses. A rough determination of ultra-violet absorption was made, neglecting reflection; but so little of the light could be concentrated on a few square millimeters of film that the thermal couple deflections resulting were very small, and hence, not particularly reliable. It was established beyond doubt, however, that up to 230 $\mu\mu$ the absorption coefficient is not very different from what it is in the blue.

Ultra-Violet Sensibility.

It appears that no quantitative measurements of the sensibility of selenium cells to ultra-violet radiation have ever been made, and it was determined to extend the sensibility curve as far as possible into the region of short wave-lengths. The source of illumination first used was an improved form of water-cooled iron arc designed by Dr. Pfund. This was found to possess such intensity that thermal couple deflections of ten to twenty-five centimeters could be obtained quite readily around 300 $\mu\mu$, while the intensity around 250 $\mu\mu$ was considerable. The arc, however, did not possess the steadiness necessary for this work and it had to give way to a quartz mercury arc, kindly lent by Professor Wood, to whom I owe my best thanks. As only a small portion of the arc could be concentrated on the spectrometer slit, the intensity obtainable was much smaller than that yielded by the iron arc, but in the matter of steadiness it left nothing to be desired.

The apparatus was set up as in Fig. 2. The lens system *L* included a water cell that cut out infra-red radiation. Screens and diaphragms cut down all diffused radiation. The concave nickel mirror M_1 focused the light of the quartz mercury arc *Q* on the vacuum thermal couple *T*, while the plane nickel mirror M_2 was arranged in a frame in such a way that it could be slid down into the path of the beam so as to divert it on to the selenium cell *C*. The cell was covered with a piece of crystal quartz cut from a plate, the remainder of which furnished the window of the thermal couple *T*. This arrangement insured that the amount of absorption was the same in each case. Experiments were carried out with two cells made by Giltay, and the results found were not essentially different. In each case, the cell was connected through the galvanometer *G* with a storage battery *B* of, usually, twelve volts. Torsion was then applied to the galvanometer suspension so as to restore the zero of the instrument to its initial position. Change of conductivity caused by a certain illumination was noted as indicated by the change in galvanometer deflection.

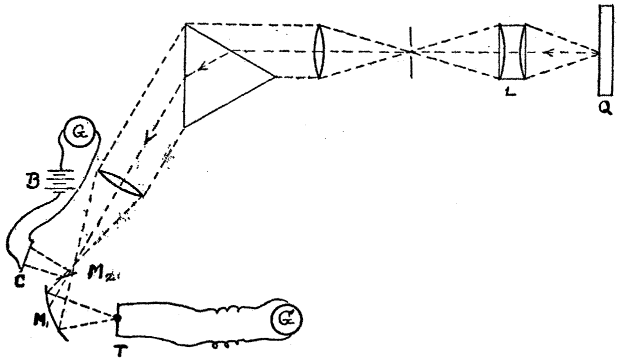

Fig. 2.

The galvanometer attached to the cell had a sensibility of 1.2×10^{-9}. It was found necessary to introduce a shunt cutting this down by a factor 3 so as to keep the deflections within the desired range. The thermal couple readings were made on the same scale, which was placed at a distance of two meters from the galvanometer.

A vacuum thermal couple was used and the chamber containing the element was joined to a vacuum[1] tube with charcoal anode, by means of which the vacuum was tested and maintained from time to time. This apparatus was kindly constructed by Dr. Pfund. The galvanometer used was one of the D'Arsonval type, and had a resistance of 20 ohms. This instrument was made by the writer. The sensitiveness of the galvanometer was 3×10^{-9} amperes while a candle placed a meter away from the thermal couple produced a deflection of 24 cm.

Limited exposure of the cell to the radiation was arranged for by using a sector rotated on the axis of the second hand of a small clock, a device used by Pfund in his latest experiments. In the same work, Pfund has shown that Talbot's law is applicable to the selenium cell, and hence, a rotating sector may be used to obtain beams of different energy. In this way, readings for unit, $\frac{1}{2}$, $\frac{1}{4}$ and $\frac{1}{8}$ energy were made. These readings indicated that the deflections for any wave-length obeyed with a very fair degree of accuracy the law

$$d = DI^{\frac{1}{2}}$$

established for the range from blue to yellow by Pfund in the work referred to above. Instead of spending much time in obtaining equal energy deflections in each case, a set of readings was made for every prominent group of lines in the Hg spectrum, using the most convenient energy readings. From these D, the change of conductivity corresponding to unit energy, was calculated, as shown in Curve 1. With each group of lines the maximum deflection for full energy was obtained. The inertia throughout the ultra-violet was observed to be small.

Sensibility Curves with Continued and with Limited Exposure.

Pfund[2] has shown that when selenium cells are exposed to monochromatic light for 12.5 sec., d, the increase in conductivity, varies with I, the intensity of the illumination, according to the law

$$d = DI^{\beta},$$

where D is a constant for any particular wave-length. β was found to be very nearly $\frac{1}{2}$ for regions of the spectrum from the violet to the yellow. As the red is approached, however, β increases; so that with deep red and infra-red $\beta = 1$. For the shorter wave-lengths, this agrees with the results found by Rosse, Adams and Berndt. This relation was tested from 230 $\mu\mu$ to 900 $\mu\mu$ and found to hold with a fair degree of accuracy.

Most of these experiments, however, were carried on in mid-summer in Baltimore, where the temperature was very high, with very consider-

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[1] See Pfund, Phys. Rev., XXXIV., 370, 1912.

[2] Phys. Rev., XXXIV., 370, 1912.

able variations and with great humidity. The results so obtained are accordingly not so reliable as would have been found under more favorable circumstances, and their agreement is not so good. Pfund, on the other hand, worked in winter, in a room in which the temperature was kept constant to one tenth of a degree. Changes in temperature are known to affect cells very markedly, while the observations of Ries and others indicate the dependence of cells on humidity. The Giltay cells are put up so that there is absolute communication between the outside air and the selenium surface, hence the variations. One cell was enclosed in an airtight box, with glass window, after it had been dried thoroughly, and thereafter it showed a marked improvement in its behavior.

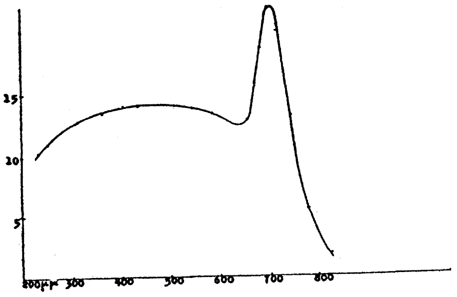

Fig. 3.

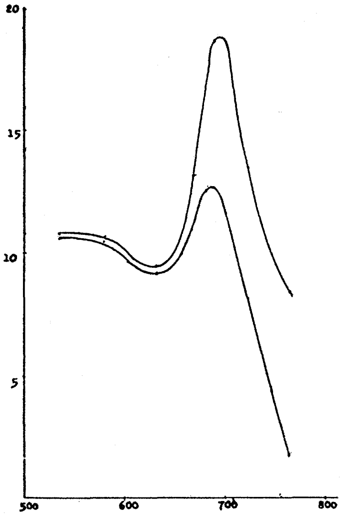

Fig. 4.

Curve 1. Sensibility of the Giltay cell extended into the ultra-violet. E.M.F. on cell, 12 volts. Time of exposure, 12½ seconds. Ordinates represent change of conductivity in terms of galvanometer deflections.

Curve 2. Showing sensibility when time of exposure was 15 seconds contrasted with the corresponding sensibility when time of exposure was unlimited. This shows the increase of inertia with the wave-length.

For the 12.5 sec. exposures the observations of Pfund were fully verified. The region in which the deflection varies as the square-root of the incident beam was found to extend into the ultra-violet, as far back as 230 $\mu\mu$. When the time of illumination was reduced to 10 sec., a noticeable increase in the value of β followed, with a small shift of the region in which β becomes 1 towards shorter wave-lengths. With the longer illuminations (15 and 20 sec.) the contrary was the result, as might be expected. Finally, with exposure until a steady state was reached, it was found that β was approximately constant and equal to .5 throughout the entire spectrum. There appeared, however, to be an appreciable minimum in the value of β about the region 600 $\mu\mu$, for here the value found in many sets of readings was about .4. The variation involved, however, may be seen to be comparatively small when we consider that it can be accounted for by a variation of less than 7 per cent. in one of the readings of deflection on which the value of β is based. The difficulties mentioned above make themselves particularly manifest here since the intervals between readings varied from about two minutes in the violet to from ten to twenty minutes in the infra-red; and as a result, conditions had an opportunity of changing very considerably during that time. If the interval between readings is not sufficiently long, fatigue makes itself manifest and the readings are affected. Curve 2 illustrates the difference between 15 sec. exposure and unlimited exposure.

Variation of Inertia with Wave-Length.

Fig. 4 shows that there is a very marked difference between the inertia of the red and infra-red as compared with the rest of the spectrum. It would be better, however, to show graphically the time required to reach say $\frac{3}{4}$ of saturation value of deflection in different parts of the spectrum, and this will be done shortly. The difference between the full deflection and that after a limited exposure is, apparently, constant from 230 $\mu\mu$ to near 700 $\mu\mu$; but here it very suddenly increases until it attains a value many times greater than before. The exact difference varies somewhat, corresponding to humidity and temperature, and very markedly to fatigue when the cell has not been allowed a sufficient rest between readings: but the general facts are always the same. This difference between the action of different parts of the spectrum led to the following experiments, suggested by Dr. Pfund.

Effects Due to a Steady Illumination Using Beams for which k is nearly Constant.

The cell was subjected to a steady illumination, first of green light, and again of deep red, and, finally, of infra-red, and sensibility curves were taken as before. This was brought about by obtaining a parallel beam of light from a Nernst glower, and throwing it on the cell by means of a right-angled prism, through a window on the apparatus covered by an absorption screen. As is the case when the current passing through the cell is great owing to a high E.M.F., so it was found here that the conductivity of the cell was very unsteady when it had been increased five to ten times by illuminating it. It was, accordingly, found necessary to interpose an inclined piece of plate glass in the path of the beam so as to cut down the conductivity to the desired degree.

In one experiment with cell No. 2, the conductivity was increased about three times by means of a beam of red light. The absorption cell used was composed of equal parts of a 10 per cent. solution of sodium bichromate and a 1 per cent. cyanine solution. This had a slight transmission throughout the spectrum but only a very little up to 710 μμ. The results found can be summed up by saying:

1. The sensibility from the violet to the orange was slightly decreased. The red maximum, however, was almost entirely cut out, and the cell became practically insensitive at about 750 μμ.

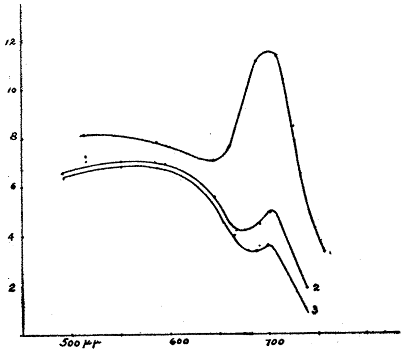

Fig. 5.

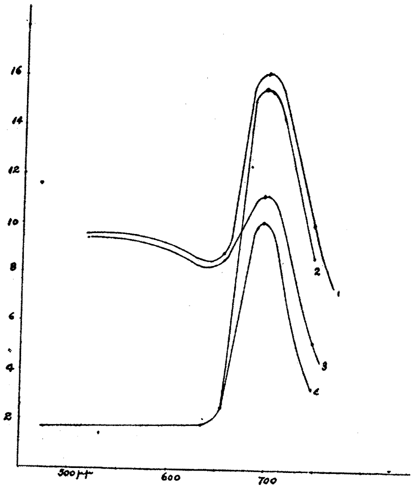

Fig. 6.

Curve 3. Cell subjected to a steady infra-red beam that increased its conductivity 2½ times. 2 and 3 show sensibility with unlimited and 15 sec. exposures, respectively. 1 gives corresponding ordinary sensibility curve.

Curve 4. Cell subjected to steady beam of green light that increased its conductivity 3 times. 2 and 4 show sensibility with unlimited exposures and 15 sec. exposures, respectively. 1 and 3 show corresponding ordinary curves. Cell unsteady. Inertia very marked in red and infra-red.

2. The inertia of the cell was very markedly decreased.

A second absorption cell whose transmission was strictly confined to the infra-red from 800 μμ to 1,950 μμ, was then used. This cell consisted of equal parts of a .6 per cent. solution of naphthol green and a 1 per cent. cyanine solution. The amount of radiation transmitted was such as to increase the conductivity about 2.5 times. The results here differed very little from those obtained using the red cell, save that the red maximum was cut out more completely and that the sensibility extended a little less far towards the infra-red. The results of this experiment are shown by Curve 3.

Finally, experiments were carried out using a saturated solution of copper chloride for the absorption cell. The transmission of this cell was not accurately determined; but it is well known that such solutions have a maximum transmission in the green while they are opaque to wave-lengths longer than .65 μ. The conductivity was now increased to three times its original value. The results that followed are shown in Curve 4, and were quite different from those hitherto obtained, for:

1. The sensibility was reduced almost to nil on the shorter wave-length side of the red maximum. The red maximum itself was reduced slightly as was the infra-red sensibility.
2. Inertia was quite marked.

Röntgen Rays.

To test further the laws stated above experiments were performed using Röntgen rays as exciting source.

To cut down the intensity of the rays by definite steps, a large rotating sector of heavy sheet lead was made. The quartz window of the cell was replaced by one of aluminum foil. By actual test, with the Röntgen ray tube in the position which it occupied throughout the experiment, the lead was of such thickness as to shield off all effects due to the rays.

A second piece of sheet lead was mounted in front of the rotating sector so as to allow only a narrow beam to strike the cell. The sector was rotated by means of an electric motor whose speed was quite high. By sliding the motor on its support, any portion of the sector could be brought in front of the hole in the lead sheet so that full, three quarters, one half or one quarter the intensity of the beam could fall on the cell.

As observed by other experimenters, the effect of Röntgen rays on the cell proved to be very slow. This rendered it an easy matter to take a reading with considerable accuracy when the exposure was of limited duration. Of course it was necessary that there should be two observers; one to observe the time, and the other to read the deflection of the galvanometer.

The results obtained from this experiment differ but little from those obtained using the long wave-lengths. With short exposures, an approximate first power law held. Exposure until a steady deflection was reached required a wait of from 15 to 30 minutes for each reading, and a still longer wait for recovery of the cell. The results indicated an approximate square root law as the following set of readings will show:

Intensity of Rays.	Deflection after 15 Sec.	Maximum Deflection.
1	3.40	11.50
2	7.70	17.00
4	15.30	24.10

ABSENCE OF SELECTIVE EFFECT.

The work of Pohl and Pringsheim on the external photoelectric effect of the alkali metals has shown that this effect depends on whether the incident light is polarized, and on the plane of polarization. Ries has found that the internal effect in selenium shows no such peculiarity through an experiment in which he allowed polarized light to fall on a cell at an angle of 45°, and observed that the deflections were of equal magnitude regardless of direction of current. A direct test of this had been made before the work of Ries was published.

A Nicol prism was introduced between the pair of lenses that focused the light of the Nernst glower on the slit of the spectrometer. A series of readings was taken throughout the visible spectrum, with the light polarized first in the plane of incidence, and then perpendicular to that plane. Suffice it to say that at no wave-length could a difference be detected between the deflection due to a given amount of energy, whether polarized in a particular plane or not. It is possible, however, that roughness of the selenium surface destroyed the polarization of the light; and to obviate this difficulty the experiment is to be undertaken with cells having mirror surfaces obtained by cathode sputtering. This observation may or may not have some value from a theoretical point of view; at any rate it seems desirable to place on record the fact that it was made.

THEORETICAL.

In the following pages an effort is made to calculate on the basis of the electron theory, the various effects that should be expected on the hypothesis put forward by Pfund that the increase of conductivity is an internal photo-electric effect. At best, such a theory can be only approximate, if extraordinary complications would be avoided. In the development of the equations, it is found necessary to leave out of account such effects as the following:

1. Variation in the coefficient of recombination. In view of the work of Plimpton[1] it is highly probable that this quantity is subject to large variation while selenium is undergoing changes due to illumination of varying intensity.

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[1] American Jl. of Sci., XXXV., 39, 1913.

2. Diffusion of the electrons. If an appreciable amount of diffusion does exist, the expression developed for the number of electrons present in a layer is inaccurate. Many experiments have shown that the absorption coefficient of metallic selenium is very high. If we take $k = 6 \times 10^4$ as the average value in the visible spectrum as obtained by Pfund, we see that the intensity of a beam of light is reduced to 1/1,000 of its initial value after penetrating

$$\frac{\log 1{,}000}{6 \times 10} = 1.1 \times 10^{-4} \text{ cm.}$$

If diffusion is not very large, then, the effective depth of penetration of the light must be much smaller than this thickness. Brown[1] has deduced from his observations that the effective depth is 1.4×10^{-3} cm. for the Giltay cell, and if his assumptions are correct, diffusion must be a large factor. Further experiments relating to this point are under contemplation.

3. "Skin effect," owing to possible thinness of layer affected by light. It is possible, however, that no serious complication would enter from such a source, as the effect would be to bring in a constant factor in the relation between number of electrons present and current flowing.

4. Variation of coefficient of absorption when conductivity is increased. Such a variation would be expected on the electron theory. However, Amaduzzi[2] found no variation in the emissivity when selenium was illuminated, and Pfund, in an unpublished research, using elliptically polarized light, could detect no change in the optical constants when the metal was illuminated by a second beam of very great intensity. This effect, if it exists, must be very small.

5. Non-uniform distribution of electrons while selenium is in the dark. It is quite probable that the density of the electrons very near the electrode is greater than elsewhere. However, this would probably introduce no serious complication.

6. Losses of electrons due to external photoelectric effect. This[3] effect is probably very small, particularly in the visible spectrum.

7. Secondary ionization.[4]

This treatment may not be fundamentally different from that which assumes chemical effects as the cause of transformations which take place in the selenium; for such transformations, in so far as they cause an increase of conductivity, mean simply a liberation of electrons. The equa-

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[1] Phys. Rev., XXXIV., 201, 1912.

[2] Accad. Lincei, XVII., 590, 1908.

[3] See Amaduzzi, Rend. di R. Accad. Bologna, XIV., 39, 1910.

[4] See Robinson, Phil. Mag., XXV., 115, 1913.

tions here given, however, possess the advantage of being in terms of quantities which have a definite physical meaning, not one purely arbitrary constant entering into the system. Accordingly, a field is opened for experimental tests which should be capable of either disproving or verifying the theory proposed.

THE VARIATION OF CONDUCTIVITY WITH INTENSITY OF ILLUMINATION.

Consider a layer of selenium whose depth is s and whose area is A. Let N denote the density of the electrons in it while in the dark. Let M^2 denote the number of electrons produced per second in unit volume, while in the dark. There will be present NsA electrons in the whole layer, and, if α^2 denote the coefficient of recombination, we have, while the selenium is illuminated

$$M^2 = \alpha^2 N^2; \quad \text{or} \quad M = \alpha N.$$

Let I denote the intensity per unit cross section of a uniform monochromatic beam of light passing normally into the surface of the selenium. Of this amount Ie^{-kx} will reach a layer a distance x from the surface, k being the coefficient of absorption. $Ie^{-k(x+dx)}$ will pass out through a surface a distance $(x + dx)$ from the top. Then j, the amount of light absorbed in the layer of thickness dx just considered, will be

$$j = AIe^{-kx} - AIe^{-k(x+dx)} = AIe^{-kx}(1 - e^{-kdx}) = AIke^{-kx}dx.$$

It is reasonable to suppose that the number of electrons expelled from their atoms due to resonance will be proportional to j—say $\mu j = \mu AIke^{-kx}dx$. There will also be a spontaneous expulsion of electrons amounting to AM^2dx in this layer whether the surface be illuminated or not. If n represents the density of the electrons in the layer there will be a loss of $\alpha^2 n^2 Adx$ due to recombination. The total change per second in the number of electrons present in the layer will be

$$\frac{d}{dt}(nAdx) = AM^2dx + \mu AIke^{-kx}dx - \alpha^2 n^2 Adx$$

So that

$$\frac{dn}{dt} = M^2 + \mu kIe^{-kx} - \alpha^2 n^2 \qquad (1)$$

$$= M^2 + c^2 e^{-kx} - \alpha^2 n^2,$$

$$= q^2 - \alpha^2 n^2,$$

c and q being introduced to reduce the mathematical complication.

The solution for this equation may be put in this form:

$$n = \frac{q}{\alpha}\left\{ 1 - \frac{2}{\dfrac{q+M}{q-M}e^{2\alpha qt} + 1} \right\}. \tag{2}$$

Now, if we denote the total number of electrons present in the whole body by m, we have

$$m = \int_0^s Andx = -A\int_{(c^2+M^2)^{\frac{1}{2}}}^{(c^2e^{-ks}+M^2)^{\frac{1}{2}}} \frac{q}{\alpha}\left\{ 1 - \frac{2}{\dfrac{q+M}{q-M}e^{2\alpha qt} + 1} \right\}\frac{2qdq}{q^2-M^2}.$$

It is seen immediately that the steady state following illumination, corresponding to $t = \propto$, is given by the first term of the integral. The second term is quite difficult to integrate; but an approximation to its value can readily be obtained if we consider the state of affairs when t has a considerable value. Then the term can be developed into a very rapidly converging series, of which the first term alone need be considered, so that

$$m = \frac{2A}{\alpha k}\int_{(c^2+M^2)^{\frac{1}{2}}}^{(c^2e^{-ks}+M^2)^{\frac{1}{2}}} \left\{ \frac{-q^2dq}{q^2-M^2} + \frac{2q^2}{(q+M)^2}e^{-2\alpha qt}dq \right\} \tag{6}$$

$$\begin{aligned} = \frac{2A}{\alpha k}\Bigg[(c^2+M^2)^{\frac{1}{2}} - (c^2e^{-ks}+M^2)^{\frac{1}{2}} + \frac{M}{2}\log\frac{M+(c^2e^{-ks}+M^2)^{\frac{1}{2}}}{M-(c^2e^{-ks}+M^2)^{\frac{1}{2}}} \\ \times\frac{M-(c^2+M^2)^{\frac{1}{2}}}{M+(c^2+M^2)^{\frac{1}{2}}} \\ - \frac{(c^2e^{-ks}+M^2)}{\alpha t\{(c^2e^{-ks}+M^2)^{\frac{1}{2}}+M\}^2}e^{-2\alpha t(c^2e^{-ks}+M^2)^{\frac{1}{2}}} \\ + \frac{(c^2+M^2)}{\alpha t\{(c^2+M^2)^{\frac{1}{2}}+M\}^2}e^{-2\alpha t(c^2+M^2)^{\frac{1}{2}}} \Bigg], \end{aligned} \tag{7}$$

neglecting all terms involving the factor $e^{-4\alpha qt}$; and since the quantity e^{-ks} is vanishingly small for cells that are opaque

$$\begin{aligned} m = \frac{2A}{\alpha k}\Bigg[\Bigg\{ (c^2+M^2)^{\frac{1}{2}} - M + \frac{M}{2}\log\frac{c^2}{4M^2}\cdot\frac{M-(c^2+M^2)^{\frac{1}{2}}}{M+(c^2+M^2)^{\frac{1}{2}}} + \frac{M}{2}\cdot ks \Bigg\} \\ - \frac{1}{\alpha t}\left\{ \frac{1}{4}e^{-2\alpha Mt} - \frac{c^2+M^2}{\{(c^2+M^2)^{\frac{1}{2}}+M\}^2}e^{-2\alpha t(c^2+M^2)^{\frac{1}{2}}} \right\} \Bigg]. \end{aligned} \tag{8}$$

After steady state has been reached, *i. e.*, when $t = \propto$, the second term has vanished. Of the first term, the quantity

$$\frac{2A}{\alpha k}\cdot\frac{Mks}{2} = \frac{MAs}{\alpha} = NAs$$

obviously represents the total number of electrons present when cell is in the dark. The increase in the number of electrons owing to illumination of intensity I then is

$$m - m_0 = \frac{2A}{\alpha k}\left[(c^2 + M^2)^{\frac{1}{2}} - M - \frac{M}{2}\log\frac{c^2}{4M^2}\cdot\frac{M + (c^2 + M^2)^{\frac{1}{2}}}{M - (c^2 + M^2)^{\frac{1}{2}}}\right]. \qquad (9)$$

If M is very small as compared with c this reduces to

$$m - m_0 = \frac{2Ac}{\alpha k} = \frac{2A\sqrt{\mu k I}}{\alpha k} = \frac{2A}{\alpha}\sqrt{\frac{\mu I}{k}}. \qquad (10)$$

As M increases in value, the proportionality between $m - m_0$ and c becomes less and less accurate.

Now, let us consider the relative value of c and M in a practical case. The number of electrons ejected by light of intensity I, according to our assumption, in an opaque layer is

$$\int_0^\infty k\mu I e^{-kx}dx = \mu I = \frac{c^2}{k}.$$

The number of electrons ejected, as indicated by the increase in conductivity, is usually of the same order of magnitude as the number produced spontaneously whether the cell is illuminated or not. Hence c^2/k is of the same order of magnitude as M^2. But, as seen, k is a very large number; hence c^2 is large compared with M^2, and in many particular cases, c will be large compared with M. We should, therefore, expect proportionality to exist between the increase in conductivity and the square root of the intensity of illumination, *i. e.*,

$$d = D\sqrt{I}.$$

This is the law verified by Rosse, Pfund, Adams, Berndt and the writer. It must be borne in mind, however, that D involves the coefficient of absorption, k, as well as μ, both of which are functions of the wavelength; hence the law will not hold for unresolved or partially resolved light. A different relation, therefore, should be expected for every source of unresolved light used. In order to obtain a complete expression connecting change of conductivity, intensity of illumination, and wavelength, it is necessary only to express μ and k as functions of the wavelength, correct I for loss of reflection, and insert its value in the equation. This problem does not at all seem hopeless.

DEPENDENCE OF SENSIBILITY ON DARK CONDUCTIVITY.

Referring to equation (9) it can readily be seen that $m - m_0$, to which the increase in conductivity is proportional, decreases as M increases.

Hence, for cells of high resistance, high sensibility would be expected. This, as a rule, is true of selenium cells. Assuming μ to be constant when the temperature is varied, we should expect a change in sensibility corresponding to temperature changes in resistance. Now μ should measure the external photoelectric effect, and this has been shown to be independent of temperature in the case of good conductors. The work of Amaduzzi[1] indicates a decrease of photoelectric effect of selenium with rising temperature, but his experiments were not carried below ordinary temperatures. However, if μ has not increased very markedly when the resistance is increased by lowering the temperature, we should expect a large increase in sensibility. This was verified by Miss McDowell[2] with a number of cells whose resistance increased several hundred times when their temperature was lowered to that of liquid air.

An experiment performed by Pochettino[3] does not admit of so ready an explanation, however. This physicist used a cell whose resistance fell very noticeably when its temperature had been lowered; but its sensibility increased somewhat, nevertheless. Cells whose resistance decreases at low temperatures are rather unusual, and to explain this effect a change in α, k or μ must be assumed.

Light-Negative Selenium.

Similar considerations lead to a possible explanation of light-negative selenium. We have, when steady state is reached,

$$m = \frac{2A}{\alpha k}\left[(c^2 + M^2)^{\frac{1}{2}} - M - \frac{M}{2} \log \frac{c^2}{4M^2} \cdot \frac{M + (c^2 + M^2)^{\frac{1}{2}}}{M - (c^2 + M^2)} + \frac{Mks}{2} \right]. \quad (11)$$

It is seen by substituting for c values of the same order of magnitude as M that the first term, representing the sensibility, is now small, while the last term, which represents the dark conductivity, is large. Now, if through the action of light α increased slightly, so that the second term would be slightly decreased, that decrease could easily be of such magnitude as to more than compensate for the first term which represents the change due to illumination. The latest work[4] on the value of α for gases indicates that when the distribution of ions is not uniform α is very much greater than it is for a uniform distribution. The impinging of light on selenium violently disturbs the distribution of electrons in the element; hence, an increase in a is plausible. Effects of this kind could not be expected to be great in agreement with the fact that the sensibility of light-negative selenium has always been found to be very small.

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[1] Rend. di R. Accad. Bologna, XIV., 39, 1910.

[2] Phys. Rev., XXXI., 524, 1910.

[3] Rend. R. Accad. dei Lincei, XI., 286, 1904.

[4] Plimpton, American Jl. of Sci., XXXV., 39, 1913.

INERTIA.

We next consider the case when t has a considerable value, but a steady state has not been reached. In such a case we have the additional term

$$\frac{2A}{\alpha^2 kt}\left\{\frac{c^2+M^2}{\{(c^2+M^2)^{\frac{1}{2}}+M\}^2}e^{-2\alpha t(c^2+M^2)^{\frac{1}{2}}}-\tfrac{1}{4}e^{-2\alpha Mt}\right\}. \qquad (12)$$

The quickness with which a steady state is reached depends on the quickness with which these terms disappear. Hence the inertia of a cell on illumination is seen to depend on the three coefficients,

$$\frac{1}{\alpha^2 k},\quad \frac{1}{\alpha(c^2+M^2)^{\frac{1}{2}}}=\frac{1}{\alpha(\mu kI+M^2)^{\frac{1}{2}}}\quad\text{and}\quad\frac{1}{\alpha M}.$$

We should expect, then, that the rate at which a maximum deflection is approached should be:

1. Least for regions of smallest absorption. This is a well-known fact, verified throughout the present work. This also explains the slow action due to Röntgen rays.

2. Least when illumination is faintest. This has been mentioned by Pfund, Miss McDowell and others, and observed by the writer again and again.

3. Least for least value of dark conductivity. This was verified by Miss McDowell,[1] who found that the action at liquid air temperatures, where the dark conductivity is very low, became very sluggish.

POSSIBLE EXPLANATION OF ANOMALOUS EFFECTS.

We have seen that in ordinary experiments c is great compared with M; hence, the effect of the second term in equation (12) will be manifest long after that due to the first. When t is very small, however, the latter is the greater term. The quantity M, on the other hand, is widely different for different preparations, from the light-negative variety up to Ruhmer's soft and hard selenium. With a suitable choice of M the first term could be made to predominate for a moment. Under such conditions, we should expect a maximum deflection to be reached in an instant, followed by a slow decrease. Effects of this kind have been observed since the earliest work done on the element.[2]

DECREASE OF INERTIA WITH STEADY RED ILLUMINATION.

An explanation of the disappearance of inertia due to red light when a cell is illuminated steadily with light of shorter wave-length can be

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[1] PHYS. REV., XXXI., 524, 1910.

[2] Ries, Die elektrischen Eigenschaften und die Bedeutung des Selens für die Elektrotechnik, p. 27.

obtained from similar considerations. Such an explanation is attempted in preference to a complete mathematical deduction owing to the great complications that arise in the solution of the equations. Here, steady illumination of the cell may be considered, on the average, with certain limitations, as being equivalent to a large increase in M. When the change in conductivity due to the incidence of a small amount of red light is then considered, we have the exponent of the first term small, since

$$c = \sqrt{k\mu I}$$

and μ is most probably small in regions of long wave-length. The two terms would, therefore, approach one another in value, so that the effect of both would be expected soon to disappear. On the other hand, the fact that μ and k are large for regions of shorter wave-length may explain satisfactorily the fact that there is no appreciable change in inertia in these regions.

Effect of Steady Illumination by Approximately Monochromatic Beam on Sensibility.

This theory is capable of development for the case just discussed when there is a steady illumination on the cell while its sensibility curve is taken. For this case the equations become extremely complicated and nothing is gained by reproducing them since a few simple considerations are sufficient to explain the facts. First, considering the case when there is a steady green illumination. As seen, we have the approximate law

$$d = D\sqrt{I},$$

D being a function of k and μ. Hence,

$$\frac{d}{dI}d = \frac{1}{2}\frac{D}{\sqrt{I}},$$

so that the sensibility to a given amount of illumination decreases as the total illumination is increased. If μ and k were constant, we should expect this decrease to be manifest throughout the spectrum, regardless of the steady illumination on our cell. But, as seen, D involves μ and k, both of which are functions of the wave-length. In regions of shorter wave-length, k being approximately constant, sensibility should disappear. In the regions of long wave-length, on the other hand, k is small. As a consequence, red light falling on a cell illuminated by green light will penetrate into its interior, to parts unaffected by green light, hence giving rise to an increase of conductivity that is almost unaffected by the presence of the green illumination.

When the cell is subjected to a steady beam of light whose coefficient of absorption is small while its sensibility is measured, the case is quite different. Obviously, the sensibility to light whose absorption is approximately the same as that of the steady beam will be very small, provided the value of μ is not very different. When a beam of light of shorter wave-length falls on such a cell, its action will be confined to a thin layer; but μ being tremendously greater here, the effect of the steady beam is hardly appreciable. This explains the retention of the blue and green sensibility when a cell is subjected to a steady beam of red or infra-red radiation.

INITIAL RATE OF CHANGE OF CONDUCTIVITY DUE TO ILLUMINATION.

Having discussed the rate of increase of deflection after light has been falling on the cell for a considerable length of time, but before the steady state is reached, it remains for us to discuss the initial rate of change. We have

$$\frac{dm}{dt} = -\frac{2A}{\alpha k}\frac{d}{dt}\int_{(c^2-M^2)^{\frac{1}{2}}}^{(c^2e^{-ks}+M^2)^{\frac{1}{2}}}\left\{\left(\mathrm{I}-\frac{2}{\frac{q+M}{q-M}e^{2\alpha qt}+\mathrm{I}}\right)\frac{q}{(q^2-M^2)}\right\}dq$$

which becomes, when $t = 0$,

$$= -\frac{8A}{k}\int_{(c^2+M^2)^{\frac{1}{2}}}^{(c^2e^{-ks}+M^2)^{\frac{1}{2}}}\frac{q^3(q+M)(q-M)^2\,dq}{(q-M)(q+M+q-M)^2(q^2-M^2)}$$

$$= \frac{A}{k}c^2 = A\mu I.$$

The initial rate of change of conductivity is, therefore, proportional to the intensity of the incident beam.

If the time considered after incidence of light on the cell be small compared with the time required to reach a maximum deflection, we should expect the change of conductivity to be approximately proportional to the intensity. When the light used is of long wave-length, or when the intensity of the beam is very small, while time of exposures is about ten seconds, then, this relation would be expected to hold. This explains the first power law established by Pfund in regions of great wave-length. Stebbins[1] assumes the same relation in his work on stellar photometry, where the intensities used were very small, and, no doubt, the law was verified by him for such cases.

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[1] Astrophys. Jl., XXXII., 185, 1910.

Recovery.

To find the expression representing the recovery of selenium, we proceed as follows:

When the illumination is cut off, there will still be produced M^2 electrons per unit volume per unit time. The rate of recombination will remain as before. Representing the density of electrons by n, as before, we have

$$\frac{dn}{dt} = M^2 - \alpha^2 n^2,$$

for which we have the solution

$$n = \frac{M}{\alpha}\left\{ 1 - \frac{2}{\dfrac{M + N'}{M - N'} e^{2\alpha Mt} + 1} \right\},$$

where N' denotes density of the electrons when $t = 0$, *i. e.*, when selenium was in a steady state under illumination.

Now, glancing at a previous equation we see that

$$N' = \frac{q}{\alpha} = \frac{1}{\alpha}\{c^2 e^{-kx} + M^2\}.$$

Having substituted this value and introduced a number of obvious approximations we obtain the solution in the form

$$m = NsA + \frac{4AM}{\alpha k}\left\{ 2 \log \frac{M\alpha + (c^2 + M^2)^{\frac{1}{2}}}{M\alpha + M} e^{-2\alpha Mt} - \frac{ks}{2}\left(\frac{1}{2} - \frac{1}{\alpha}\right) e^{-2\alpha Mt} \right.$$
$$\left. + \frac{1}{\alpha} \log \frac{c^2}{4M} \cdot \frac{M + (c^2 + M^2)^{\frac{1}{2}}}{M - (c^2 + M^2)^{\frac{1}{2}}} e^{-2\alpha Mt} \right\}.$$

The deductions to be made from this are not greatly different from the results of the former equation, viz.,

1. Rate of recovery greatest when absorption is greatest, amply verified by experiment.
2. Rate of recovery greatest for great values of I and μ.
3. Rate of recovery greatest with cells of high conductivity, a fact often observed and verified by Miss McDowell in her low temperature experiments.

Glancing at the terms involving t, we see that that quantity appears only in the expression $e^{-2\alpha Mt}$. Moreover, this quantity is associated with coefficients of considerable magnitude. Turning to equation (8) on the other hand, we see that the term controlling the time required to reach a steady state under illumination is $\frac{1}{2\alpha^2kt}e^{-2\alpha Mt}$. The latter, therefore, disappears much more quickly than the former. This is in agreement with experiment, for it is well known that it takes a longer time to return to the initial conductivity after a cell has been illuminated than it does to reach a steady state under illumination.

BEARING ON EFFECTIVE DEPTH OF PENETRATION.

The agreement between the above deductions and experiment indicates that the view expressed is correct that μ increases with decreasing wave-length. The only experimental evidence on this point is the work of Amaduzzi[1] who found that μ had a value in the ultra-violet but that it was too small to be measured in the visible spectrum. As seen, the approximate sensibility law is

$$d = D\sqrt{I},$$

where D is a function only of μ, α, and k. Moreover, k is nearly constant on the short wave-length side of 550 $\mu\mu$. This law would, accordingly, require a steady increase of sensibility as μ increased, and this is not borne out by experiment. It would seem, then, that a factor not taken into account in the above discussion enters into the problem. This strengthens the view of Pfund that the effective depth of penetration is so small here that Ohm's law fails to hold and it is necessary to introduce an undetermined factor in the relation between conductivity and number of electrons present.

TIME TAKEN IN REACHING A STEADY STATE.

The equations given above fail to represent the facts concerning the time taken to reach a steady state under illumination. The equations would indicate that this should be extremely short—less than a second, in an average case, probably. As a matter of fact, the time required by a selenium cell to reach a steady state is considerable, varying from about 20 seconds to several hours. It is probable that a distinction should be made between lag proper to the selenium owing to the change in conductivity caused by the illumination and the lag, due to Joule heating, and potential effects. At best, however, a considerable disparity exists on this point. A plausible explanation of it may be found in the fact that diffusion has been neglected in the development of the equations. Even if diffusion were so small that its effect had little influence on the general conclusions derived from the equations, it is quite possible that,

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[1] Rend. di R. Accad. Bologna, XIV., 39, 1910.

if its influence be taken into account in the latter, the time required to reach a steady state would be found to be lengthened considerably.

When this factor is taken into account, equations result as given below, for which a solution has not yet been obtained. Let n' denote density of atoms that have lost an electron, and C, the coefficient of diffusion of electrons. The reasoning used above will apply here, so that we have

$$\frac{\partial n'}{\partial t} = M^2 + c^2 e^{-kx} - \alpha^2 nn'.$$

For electrons the equation will be somewhat different. $AC(\partial n/\partial x)$ electrons will enter the layer considered above through the top surface, in unit time. $AC[(\partial n/\partial x) + (\partial^2 n/\partial x^2)dx]$ will pass through the lower surface. The layer will gain, accordingly, $-AC(\partial^2 n/\partial x^2)dx$ electrons in one second, and we should have

$$\frac{\partial n}{\partial t} = M^2 + c^2 e^{-kx} - \alpha^2 nn' - C\frac{\partial^2 n}{\partial x^2}.$$

Summary.

1. Considerable information has been collected regarding the sputtering of selenium cathodes, and an improved form of sputtering apparatus has been used.

2. Many semi-transparent films of amorphous selenium have been transformed into the metallic state.

3. The ultra-violet absorption of metallic selenium was roughly determined.

4. Selenium cells have been found to retain a large sensibility down to 230 $\mu\mu$, and the sensibility curve for short wave-lengths was determined.

5. Sensibility curves were obtained when exposure was limited and of varied duration, as well as when steady state was reached. If change in conductivity be represented by d, energy of incident beam by I, while β and D are constants, the law $d = DI$ was found to hold with considerable accuracy in every case. When exposure is between 12.5 sec. and 20 sec. Pfund's results are confirmed that $\beta = 1$ in red and infra-red but $\beta = \frac{1}{2}$ for shorter wave-lengths. For unlimited exposures it was found that $\beta = \frac{1}{2}$ throughout the spectrum·

6. Sensibility curves were obtained with a cell permanently exposed to illumination of different wave-lengths, and different peculiarities were noted.

7. The law $d = DI^\beta$ was found to hold with considerable accuracy when the exciting source was Röntgen rays. For short exposures, $\beta = 1$, while $\beta = \frac{1}{2}$ when time of exposure is unlimited.

8. Experiments conducted with home-made cells indicate that they obey the same laws as the Giltay cell.

9. A mathematical deduction has been made, with the electron theory as a basis, from which the most important facts known regarding the behavior of selenium cells have been deduced. The facts accounted for are as follows:

(*a*) Variation of change in conductivity with square root of intensity for long exposures.

(*b*) Variation of change in conductivity directly with the intensity when time of illumination is short compared with that required to reach a steady state.

(*c*) High sensibility of cells of high resistance.

(*d*) Decrease of inertia with increasing intensity of illumination, absorption coefficient, and "dark conductivity." This also explains variation of sensibility with temperature and other disturbing factors.

(*e*) Dependence of rate of recovery upon the same causes.

(*f*) Change in sensibility when cell is illuminated continuously with a beam of light for whose constituents k is nearly constant.

(*g*) Decrease in inertia when this beam is red, or infra-red.

(*h*) Possible explanation of "light-negative" selenium and anomalous effects.

In conclusion I beg leave to express my best thanks to Professor Ames and the entire staff of the physical laboratory of the Johns Hopkins University for interest taken in the work; also to Mr. S. M. Burka, who assisted me in the construction of apparatus and in taking readings. I feel that special mention should be made of Dr. Pfund, who suggested the work and spared no pains in aiding me in every possible way.