THE TIME FACTOR IN SELENIUM RESISTANCE.

By G. E. Grantham.

EARLY observers of the light action of selenium discovered that the electrical resistance of selenium does not reach an equilibrium value instantaneously after exposure to light, and that the rate of change of resistance on exposure is much greater than the recovery rate.

A large amount of material has been published showing the relation between time of exposure and the resistance of the selenium cell;[1] and the effects of various agencies, such as pressure,[2] wave length of light to which the selenium was exposed,[3] temperature of the cell,[4] Röntgen radiation,[5] etc. A few observers have investigated the recovery of the selenium cell during the fractional part of a second following exposure. Since this field has not been entirely covered by experiment the present work was undertaken.

The problem suggested the use of a rotating disk from which sectors had been cut to allow the light to fall upon the cell, the cell to be in one arm of a Wheatstone bridge with some device for connecting a galvanometer in the bridge circuit at a known time interval after exposure. This method introduced the necessity of a preliminary experiment to determine the effects of different speeds of the disk on the change of resistance of the cell.

Preliminary Experiment.

A selenium cell, connected in one arm of a Wheatstone bridge, was placed in a light-tight box, the inside of which was coated with lampblack and shellac. A piece of iron pipe of 5 cm. diameter and 60 cm. long was fitted closely in a hole in one end of the box. A cap which had an opening in it the exact size of one of the sectors was placed over the outer end of the pipe. The rotating disk of 45 cm. diameter was mounted at right angles to the pipe on a shaft to which was attached a speed counter and a small electric motor. Two sectors diametrically opposite were cut from the disk permitting the cell to be exposed twice each

[1] F. C. Brown, Phys. Rev., XXXII., p. 252; XXXIII., p. 406, 1911.

[2] F. C. Brown and Joel Stebbins, Phys. Rev., XXVI., p. 273, 1908.

[3] Pfund, Phys. Rev., XXVIII., p. 324, 1909.

[4] Miss Louise MacDowell, Phys. Rev., XXXI., p. 529, 1910.

[5] G. Athanasaidis, Ann. d. Physik, 27.4, p. 890.

revolution. The disk was rotated at 215, 690 and 1,200 R.P.M. A one candle power incandescent lamp was placed near the disk and used as the source. The result of these observations is shown graphically in Fig. 1.

The preliminary experiment showed that there was a variation in the resistance of the cell with change of speed of the disk, although the quantity of light falling upon the cell was the same at all speeds. However, this change of resistance was so slow that it could not interfere essentially with the observations taken by the proposed method.

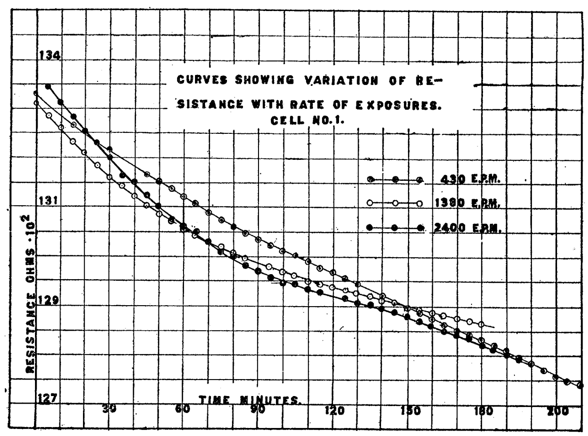

Fig. 1.
Exposures made to a 1 c. p. incandescent lamp.

The apparatus constructed for the study of the resistance change during a short interval was as follows: A small hard rubber disk of 5 cm. diameter and a metal disk of 45 cm. diameter were mounted on the same shaft of a motor equipped with a speed counter. In the circumference of the rubber disk, 90 degrees apart, were inlaid four brass cylinders of 0.8 cm. diameter. The diametrically opposite cylinders were connected in pairs by brass strips on the side of the disk. Two brushes were mounted on a wooden block which was separate from the remainder of the apparatus and yet free to rotate about the same axis as the disk. A pointer attached to the axis of the brushes moved over a fixed graduated disk and served the double purpose of indicating the angle of lead or lag of the brushes with respect to the sectors and of clamping the brushes in any desired position. The brushes were connected in the galvanometer circuit of a Wheatstone bridge. The two galvanometers used at different parts of the study were of the d'Arsonval type, one having a figure of merit of 0.83×10^{-9} amperes per mm. for a distance of

212 cm. between the scale and mirror. The other was not as sensitive. A single storage cell was used as the battery. The selenium cell was placed in the light-tight box previously described and connected in the Wheatstone bridge circuit.

The selenium cell used in the preliminary experiment was one of the Bidwell type[1] bought from Max Kohl and will be designated as Cell No. 1 throughout this paper. Three selenium cells were used for the second part of the experiment. Cell No. 1 had a sensitiveness of 1.0 : 1.5 (ratio of change of resistance to dark resistance). Cells *22B* and *50C* were made by Giltay. The sensitiveness of *22B* was 1.0 : 1.4 and that of *50C* was 1.0 : 2.2. The dark resistances of Nos. 1, *22B* and *50C* were 35,000, 290,000 and 20,000 ohms respectively. The cells frequently became almost insensitive. By connecting a cell in series with two spark gaps, two Leyden jars in multiple and a 3 in. spark induction coil and sending oscillatory discharges through the cell for about five minutes the sensitiveness was generally restored. The cell would be in a very unsteady state of equilibrium for a day following such treatment.

For illumination a Nernst lamp, the terminals of which were kept at a constant voltage, was used for a part of the experiment and a Welsbach burner for the remainder.

Method of Taking Observations.

The apparatus was so arranged that when the indicator on the graduated circle pointed to zero the galvanometer was thrown in the circuit at the same instant as that at which light fell upon the cell. If the indicator pointed to 10 degrees, the galvanometer was thrown in the circuit at a time later than the exposure equal to the time required for the disk to rotate through 10 degrees. The speed of rotation was given by the speed counter and this time interval was easily calculated. A separate switch served the purpose of throwing the commutator out of the bridge circuit. The brush contacts were tested in this manner.

Results.

The relation between time and resistance for the preliminary experiment is shown in Fig. 1. It is seen that during the first hour the rate of change of resistance increased with the speed. For a speed of 215 R.P.M. the resistance change during the first hour was 210 ohms, for a speed of 690 R.P.M. the change was 260 ohms, and for a speed of 1,200 R.P.M. the change was 310 ohms. During the remainder of the time the cell approached the equilibrium resistance. This equilibrium

[1] Shelford Bidwell, Proc. Phys. Soc., London, Vol. XI., p. 61.

resistance is the resistance of the cell at the time that the decrease on exposure is just equal to the increase in the dark. It is evident from the

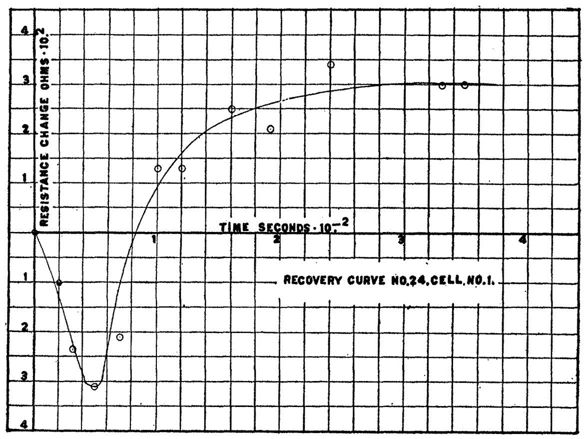

Fig. 2.

Exposures made to a Nernst lamp at a distance of 60 cm. Speed of disk, 490 R.P.M.

curve that the equilibrium resistances will not be equal although the total quantity of light falling upon the cell is the same.

Figs. 2 to 5 show the results of the experiment proper. The loops in curves below the X axis apparently indicate that the resistance of the

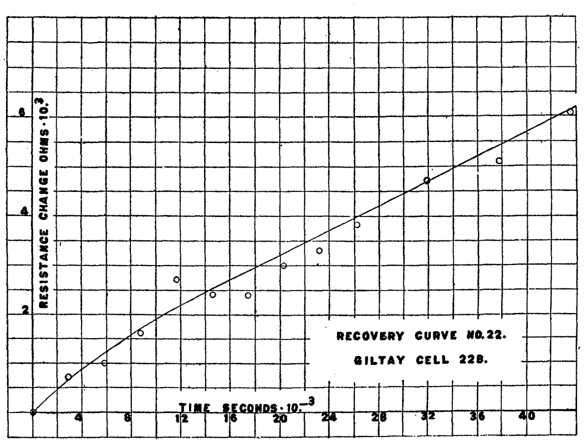

Fig. 3.

Exposures made to a Welsbach burner at a distance of 70 cm. Speed of disk 560 R.P.M.

cell a short time after exposure was less than the resistance when the cell was actually exposed to the light. It was first thought that this negative loop might be caused by some contact electromotive force at the brushes and an auxiliary experiment was performed by substituting for the hard rubber disk a commutator made of two brass rods set at right angles to each other. Brushes made of the same material as the commutator were used. Then a resistance of the same magnitude as that of the selenium cell was introduced in the circuit, by reversing a switch which at the same time cut the selenium cell out of the circuit. No negative loop appeared and it was concluded that the loop was due to some change within the cell.

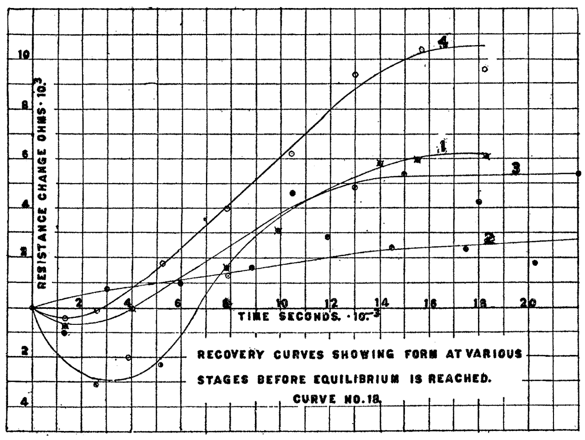

Fig. 4.

Exposures made to a Welsbach burner at a distance of 70 cm. Speed of disk for curves Nos. 1, 2, 3 and 4, 1200, 560, 1250 and 2400 R.P.M. respectively.

The negative loop did not appear if the readings were obtained within a very short time after the first exposure, as shown in Fig. 3. If the motor was run for an hour or longer before the readings were taken, a pronounced negative loop was obtained, as shown in Fig. 2. Fig. 4 shows some of the many various forms of curves obtained. Curve No. 1 was obtained when the cell had reached its equilibrium value.

Discussion of Results.

The results of this experiment can be explained if it be assumed[1] that selenium consists of three components, A, B, and C, which under the action of light change according to the reaction; $A \rightleftharpoons B \rightleftharpoons C$. Assume that the resistivity of the component A is infinite, that of B approaches the resistivity of metals, and that of C has a value near that of A. Assume, further, that component A changes to B at the rate a_1, B changes

[1] F. C. Brown, Phys. Rev., Vol. XXXIII, p. 1, 1911.

to C at the rate b_1, that the respective reverse rates are a_2 and b_2, and that the rate a_1 is much greater than the rate b_1. Then for a very short exposure some of A changes to B, but very little of B changes to C. During the recovery period between exposures, which is approximately thirty times as long as the time of exposure, some of C will change to B and some of B will change to A, but as the recovery rate is slow compared to the changing rate for one exposure, so for very short repeated exposures there will be a larger transformation to B than for longer repeated exposures. The resistance of the selenium cell depends upon the amount of B present and consequently for a time the rate of change should be greater for short exposures. The differences in the equilibrium values are due to the different amounts of B present.

In accordance with this hypothesis, the negative loop in Figs. 2 to 5 is easily explained. For a single short exposure, A changes to B, but very little of B changes to C. The change of C to B for a single short exposure can be neglected, but for repeated short exposures more and more of B changes to C, so that a longer time will be required for recovery. After the machine has been running for a time, a certain amount of B will change rapidly to C on exposure and then change slowly from C to B in the dark. Obviously there will be an apparent negative change due to the lag of the $B \leftarrow C$ change behind the $B \rightarrow C$ change. The curves of Figs. 2 to 5 then give a difference value between exposure and recovery values.

The equation of the resistance-time curves will have constants depending upon the rates of change a_1, a_2, b_1 and b_2. The conductivity will depend upon the amount of B present and F. C. Brown[1] has shown the relation to be given by the equation

$$i = K(L/N + C_1 e^{m_1 t} + C_2 e^{m_2 t}), \tag{1}$$

in which L, N, C, m_1, C_2 and m_2 are constants which depend upon the rates of change of the components. By writing five equations using different values for t the constants may be eliminated. For convenience the substitutions $x = e^{m_1}$ and $y = e^{m_2}$ were made. The final equation then is:

$$\frac{y^2(i_2 - i_1) - (i_4 - i_3)}{y^2(i_1 - i_0) - (i_3 - i_2)} = \frac{y^2(i_1 - i_0) - (i_3 - i_2)}{y(i_1 - i_0) - (i_2 - i_1)} - y, \tag{2}$$

in which i_0, i_1, i_2, i_3, and i_4 are the values of the conductivity at times t_0, t_1, t_2, t_3, and t_4 respectively. By choosing values of x and y the constants for a family of curves may be calculated, giving the various forms of the curves between the equilibrium value of the cell and the condition

[1] Loc. cit.

existing after the first few exposures. The constants for a family of such curves are given in Table I. The equation which most nearly represents curve No. 3 of Fig. 4 was found by a cut and try process to be:

$$i = 1017 + 4005e^{-3 \cdot 21t} + 4063e^{-2 \cdot 91t}. \qquad (3)$$

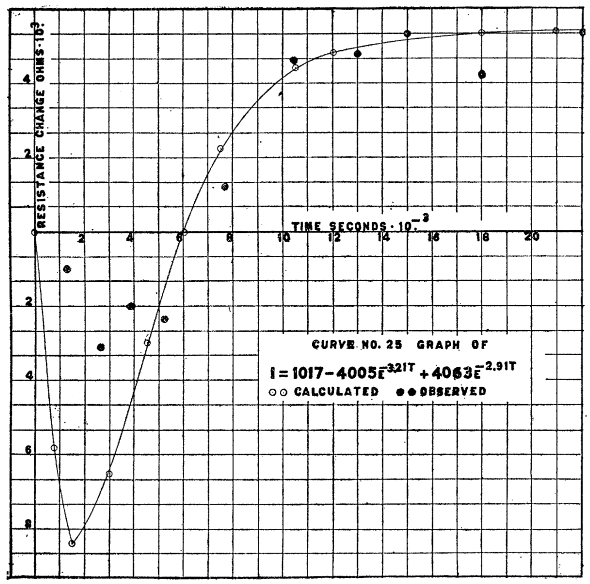

Fig. 5.

Comparison of theoretical and experimental data.

This equation is shown in graphical form in Fig. 5 together with the points experimentally determined. It is seen that beyond four one thousandths of a second the curves are almost identical. No values of

TABLE I.

Values of the Constants upon which the Rates a_1, a_2, b_1 and b_2 depend.

x	y	L/N	C_1	C_2	m_1	m_2
0.0343	0.06	1,017	− 2,121	2,179	−3.4	−2.82
0.0243	0.07	1,017	− 1,188	1,246	−3.74	−2.66
0.0373	0.057	1,017	− 2,788	2,846	−3.3	−2.87
0.0443	0.05	1,017	− 9,666	9,724	−3.12	−3.0
0.0463	0.048	1,017	−32,480	3,253.8	−3.08	−3.04
0.0423	0.052	1,017	− 5,668	5,726	−3.17	−2.96
0.0403	0.054	1,017	− 4,005	4,063	−3.21	−2.92[1]
0.0393	0.055	1,017	− 3,491	3,549	−3.24	−2.9
0.0143	0.08	1,017	− 812	870	−4.33	−2.52
0.0043	0.09	1,017	− 615	673	−7.68	−2.4

[1] Values chosen for equation (3).

x and y which give finite values for the different rates will make the curves compare favorably below four one-thousandths of a second. Then if the general equation for conductivity holds it is evident that the curve should reach a minimum a very short time after exposure. The theory offered explains this. For a very short exposure there will be a change $A \rightarrow B$. Since the rate a_2 is smaller than the rate a_1, if the galvanometer be thrown in the circuit in such a short time following exposure that but little of $A \leftarrow B$ change has taken place, the resistance must be lower than when measured during the exposure, for a_1 is finite and at a speed of 500 R.P.M. the time of exposure is less than one thousandth of a second. The effect of the C component will not enter for every short exposures. Because of the time of contact of the brushes, the time interval following exposures could not be measured to a greater degree of accuracy than two thousandths of a second. This explains why the curves plotted from experimental values do not have a minimum nearer the ordinate.

The results of these experiments are in accord with the three component theory of selenium.

It is intended, in a later paper, to show the variation of resistance of a light-negative cell under similar conditions.

This investigation was suggested by Professor Arthur L. Foley and I wish to thank him for his kindly interest and direction during the course of the experiment. I wish also to thank Dr. R. R. Ramsey for his many helpful suggestions.

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