THE NATURE OF ELECTRIC CONDUCTION AS REQUIRED TO EXPLAIN THE RECOVERY OF RESISTANCE OF METALLIC SELENIUM FOLLOWING ILLUMINATION.

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DIFFERENT theories have been proposed to explain the transportation of electricity in solids, but metallic conductors generally have not offered satisfactory evidence for a final decision between the theories. The illuminating experiments on thermionics by Richardson and his students and also the consistent agreement of theory and experiment involving the ratio of the electrical to the thermal conductivity of metals have made various modifications of the dynamical equilibrium theory very popular. The seemingly most contradictory evidence to this theory is the low value of the specific heat for all the metals. However, Sir J. J. Thomson[1] has shown that the calculated and experimental ratios of the electrical to the thermal conductivity may agree equally well by a theory that presumes the electrons to be tied up with the atom in the form of a doublet. In this case electric conduction would be merely the transportation of electron from doublet to doublet much in the same way as the Grotthus chains in the old theory of electrolysis.

I shall in this paper present information which leads away from the first mentioned view above and which forms the basis for a theory bearing more or less resemblance to the above mentioned second theory of Thomson. For the reason that the conducting power of metallic selenium crystals may be varied by so many physical conditions, we have the obvious opportunity of making very definite choice as to what form of the electron theory is satisfactory. Having obtained a consistent theory for selenium, we can then decide if reasonable modifications of the theory will explain conduction in the other elements, where there are less favorable means of attack.

The investigations described in this and succeeding papers will be somewhat along the line of attack made by J. W. Nicholson.[2] An effort will be made to choose experiments that enable decision to be made with

[1] Book on the Corpuscular Theory of Matter, 1907.

[2] PHYS. REV., N. S., Vol. 3, p. 1, 1914. See also article by Merritt, PHYS. REV., 25, p. 505, 1907, which involves some of the elements of the ideas in this paper.

a minimum number of assumptions. The author is not aware of any direct or indirect measurements having been made which consider any particular value for the rate of recombination of electrons with their positive residues, except in the conduction of electricity through a gas under the influence of an ionizing agent. The subject will be opened by a consideration of the rate of recombination of the electrons and some of the conditions that influence this rate.

THEORETICAL CONSIDERATIONS.

It will be assumed that the specific conductivity varies as the number of electrons taking part in the conduction at any instant. The electrons do not exist free in the sense of the kinetic theory of gases. Under illumination they are rendered unstable or free but on the average they recombine with the atomic structures very rapidly. Experiment shows that following intense illumination thirty per cent. of the extra electrons return to their fixed positions in .02 second. A second assumption that will be made is that the recombination of the freed electrons will take place according to the same law governing the recombination of ions in gases. Then the rate of recombination of electrons will be expressed as,

$$\frac{dN}{dt} = -\alpha N^2, \tag{1}$$

where N is the average number of electrons in the free state at any instant and α is the coefficient of recombination. However, this equation holds only for a uniform distribution of the electrons. Such a distribution would exist when the selenium reaches the equilibrium condition in the light, or for the first small interval of time, Δt, after the illumination is shut off. The theory will presuppose that the coefficient of recombination is not altered by the condition of light or dark, and the experiments will verify this presumption.

Since the conductivity is proportional to the number of free electrons, we may write,

$$i = k_1 \cdot N \tag{2}$$

from which it follows that

$$\frac{di}{dt} = -\frac{\alpha i^2}{k_1}, \tag{3}$$

or

$$\frac{di}{dt} = -\alpha' i^2,$$

where α' is merely a new constant.

When the selenium is in equilibrium in the light the rate of recombination of the electrons is exactly equal to the rate of production of

electrons by the light in addition to the natural production in the dark. This may be represented as

$$\frac{dN}{dt} = M + q,$$

or

$$\frac{di}{dt} = k_1(M + q), \tag{4}$$

where M is the former rate and q is the latter or dark rate. Combining equations (3) and (4) we obtain, for the equilibrium value of the current,

$$i_e = k_1\sqrt{\frac{M + q}{\alpha}}. \tag{5}$$

Now we could check the theory by the application of observed data to satisfy equation (5), but the rate of production of electrons by light, M, is dependent upon the light intensity and therefore it will be more convenient to test the adequacy of the equation in the next succeeding paper, together with the law governing the rate of production with varying light intensities. It will be the purpose of this paper to verify the fundamental relation of rate of recombination to the number of free electrons, as expressed in equations (1) and (3). It was found that equation (3) could be verified when expressed in the approximate form

$$\frac{\Delta i}{\Delta t} = -\alpha' i^2, \tag{3}$$

when Δt was kept a very small interval of time and constant. Ordinarilly we should expect to check this equation by the application of its integrated form,

$$\left(\frac{1}{i} - \frac{1}{i_0} = \alpha t\right)$$

to a complete recovery curve extending over a considerable length of time. However, I have found that this can not be carried out satisfactorily because as soon as a large percentage of the electrons have recombined, a non-uniform distribution of the electrons and uncombined atoms exists, such that the coefficient of recombination is diminished. But it is not essential to the argument of this paper to either prove or disprove this statement. A slow diffusion of the electrons, and changing crystalline structure, no doubt are complexities to be taken into account in explaining a complete recovery curve.

That equation (3) is tenable, together with the underlying assumptions mentioned, may be ascertained from some observations taken with masses of crystals some years back. In my paper on the " Recovery of the Giltay Selenium Cell and the Nature of Light Action in Selenium "[1] on p. 415

[1] PHYS. REV., Vol. 33, p. 403, 1911.

is just such data as desired. The conducting component, B, has the same significance as i or N in this paper. The recovery during the mean interval of .05 second was measured after the selenium had begun to recover from illumination of varying intensities. The varying intensity produced the varying conductivity noted in the following table.

Conductivity in Dark. i_0	Conductivity in Light. i	Change of Conductivity, Ohms^{-1}. $\Delta i = k \cdot N$	$\frac{\Delta i}{i}$	$\frac{\Delta i}{i^2}$	Coefficient of Recombination. $\alpha' = \frac{\Delta i}{i^2 t}$
1.47×10^{-6}	6.29×10^{-6}	0.016×10^{-5}	2.5×10^{-2}	4.0×10^{3}	80×10^{3}
	$13.5 \times$ "	$0.11 \times$ "	$8.2 \times$ "	$5.9 \times$ "	$118 \times$ "
	$60.2 \times$ "	$2.79 \times$ "	$46.5 \times$ "	$7.6 \times$ "	$152 \times$ "
	$35.4 \times$ "	$1.05 \times$ "	$29.6 \times$ "	$7.9 \times$ "	$158 \times$ "
	$50.8 \times$ "	$2.04 \times$ "	$40.2 \times$ "	$7.4 \times$ "	$159 \times$ "
	$16.1 \times$ "	$0.18 \times$ "	$11.2 \times$ "	$6.9 \times$ "	$138 \times$ "

It may be observed, where the change of conductivity varies over the extreme range of from .016 to 2.79 (*i. e.*, by a factor of 174) that $\Delta i/i^2$ is approximately a constant. The values of α' as recorded in the last column are slightly in error because no allowance is made for the liberation of electrons taking place in the dark simultaneously with their recombination. If no new postulates are involved this correction should be of magnitude, $(i_0^2 \cdot \alpha' \cdot \Delta t)$, when added to Δi for the calculation of α'. Since this correction involves an error of less than ten per cent. in any value above, we will not complicate the argument of this paper by the application of this correction or considerations of the adequacy of the correction. Since the range of application of the data is so great, we may regard the constancy of the coefficient of recombination as satisfactory evidence that the electrons recombine with the atomic structures in accordance with the conception involved in equation (1), when the conditions are as specified. Since writing this paper I have also verified this fundamental conception by experiments on the recovery of single isolated crystals of selenium. This agreement of behavior of crystals and crystal aggregates is quite consistent with the other unique properties existing in the crystals, such as the likeness of the wave-length,—sensibility curves.[1]

It may be noted that a constant coefficient of recombination involves the idea that the number of electrons freed in dark recombine at a more rapid rate, when the selenium is illuminated or just following illumination. This follows because there are more positive residues and consequently more chances for recombination.

It should also be noted that Plimpton[2] has observed that ions in gases

[1] PHYS. REV., N. S., Vol. 4, p. 507, 1914; Vol. 5, p. 65, 1915.

[2] Am. Journ. of Sc., Vol. 35, p. 39, 1913.

also recombine according to the same law involved in equation (1), only in case there is a uniform distribution of ions. However, this agreement of the law of recombination of electrons in selenium with the recombination of ions in gases does not further lead us to suspect that the electric current may be transported by the same method in both selenium and in gases. The current in selenium with a given low potential is infinitely larger than any ionization current in gases, except in spark discharge. Further differences and likenesses of the method of transportation of the current will be brought out in later developments of the theory.

THE INADEQUACY OF OHM'S LAW.

A fundamental property in metallic selenium exists in the inadequacy of Ohm's Law to explain the variation of the current with the applied voltage. In all cases the current increases more rapidly than the proportional increase of the voltage. It is therefore pertinent to inquire what conditions are responsible for this unique property. According to the theory involved in equation (5) an increased potential can vary the specific conductivity only in two ways, by varying the rate of production of the electrons or by varying the rate of recombination of the electrons.

We will suppose that the increase of current necessary to satisfy Ohm's Law, when the voltage is increased, arises from increased velocity of drift of the electrons, and that the slight excess current arises from additional electrons in the conducting state. This increased number might come either from a magnified rate of production or from a diminished rate of recombination.

The increased rate of production might be expected because of bombardment of semi-fixed electrons by the faster moving ones or the greater electric intensity might be considered as lowering the degree of stability of all the electrons of a certain class in the atomic structure. Consistent with either of these views, it would be reasonable to expect a diminished rate of recombination as the voltage is increased. An increased velocity of drift would lessen somewhat the chance of an atom to capture an electron and also a lower stability of the atom would indicate a smaller attractive force for the electron.

A measurement of the recovery during a short interval following the extinction of the illumination should determine whether the coefficient of recombination varies with the applied potentials in such a manner as to explain the inadequacy of Ohm's Law.

The change of conductivity during short periods of recovery was measured by the Wheatstone's bridge and pendulum method.[1] The light

[1] PHYS. REV., Vol. 33, p. 54, 1911.

was cut off the selenium at the desired time by an aluminum shutter attached to the timing pendulum. A single lamellar crystal of metallic selenium of the fifth system was used for this investigation. The intensity of illumination from which the crystal recovered was kept constant. Also the pressure on the crystal was fixed at such a value that the resistance was 1,349,000 ohms with 1.45 volts. The change of conductivity was measured for the first 0.05 second interval of recovery, both when 1.45 volts was the difference of potential across the crystal and when there was 20 volts.

The change of conductivity during recovery of 0.05 seconds is shown in the following table. For convenience 0.05 second is here considered as the unit of time.

	With 20 Volts.	With 1.45 Volts.
Resistance in dark	1,192,000	1,349,000
Resistance in unvarying light	356,000	392,000
Conductivity in light	$i = 28.1 \times 10^{-7}$	$i = 25.5 \times 10^{-7}$
Recovery after 0.05 second	$i = 15.65 \times 10^{-7}$	$i = 14.1 \times 10^{-7}$
Change of conductivity	$\Delta i = 12.5 \times 10^{-7}$	11.4×10^{-7}
$\alpha' = \frac{\Delta i}{\Delta t \cdot i^2}$	1.58×10^5	1.75×10^5
$\frac{\alpha'}{i} = \frac{\Delta i}{i} = \frac{\Delta N}{N}$	0.447	0.447

It may be observed that the coefficient of recombination is not constant. In fact a brief consideration of the data reveals that this coefficient varies directly as the specific resistance of the crystal, when the variation of the specific resistance accrues from an altered potential difference between the crystal electrodes. This conclusion is verified by the constant ratio of α'/i, as recorded in the last row above.

If the constant, α', were the sole quantity that changed its value with varying potentials across the crystal, then we might expect in accordance with equation (5) that the equilibrium light sensitiveness of the crystal would vary inversely as the square root of α. However, the data for the same crystal that is given in the following table shows that the equilibrium light sensitiveness is almost proportional to the conductivity in the light. Since (α) varies inversely as the same conductivity in the light, and since the conductivity is influenced only by the square root of the recombination constant, it follows that the light sensitiveness should, according to equation (5), vary directly by some function of $M + q$, and further that this function should have the same value as the function relating (α) to the conductivity. This idea is a little beyond the province of this paper and will need to be verified further.

Potential across the crystal in volts	1.5	6.0	36	60
Conductivity in dark	5.9×10^{-7}	6.0×10^{-7}	6.85×10^{-7}	7.5×10^{-7}
Conductivity in light	20×10^{-7}	20.4×10^{-7}	23.3×10^{-7}	24×10^{-7}
Equilibrium light sensitiveness	14.1×10^{-7}	14.4×10^{-7}	16.5×10^{-7}	$16.5 - 10^{-7}$
$\frac{\text{Light sensitiveness}}{\text{Conductivity in light}}$	.705	.70	.70	.69

THE PRESSURE EFFECT.

The increase of the specific conductivity of selenium, by pressure, whether in isolated crystals or crystal aggregates is another unique principle that our electron theory should explain.[1] The specific conductivity may vary a hundred fold by increasing the pressure. According to the postulates in the earlier part of the paper, this increase of conductivity must arise either from an increase in the number of electrons capable of taking part in the conduction or in a decrease in the ratio of recombination of the electrons with the positive residues. From a consideration of the increase of the absolute light sensitiveness with increased pressure I have already concluded[2] that it would be unreasonable to expect the light-sensitiveness to increase in proportion to the conductivity in the dark, if the conductivity must vary alone with the number of electrons liberated.

Since there is no reason to expect any large changes of conductivity resulting from variations in the free path of the electron, it seemed very plausible that pressure might alter the rate of recombination of the electrons.

In the experimentation, the selenium crystal was placed between brass electrodes and the variable pressure desired was controlled by a screw adjustment. At each pressure the equilibrium conductivity was measured both with the crystal in the dark and with constant illumination. The recovery was measured during the first mean period of .02 second after the extinction of the illumination as elsewhere described. A constant difference of potential of 13 volts was kept between the crystal electrodes. The equilibrium conductivity in the light was attained in less than a second after illumination.

The following table shows the value of the coefficient of recombination for various pressures on the crystal such that the conductivity varied from 1.79×10^{-7} to 23.8×10^{-7} in the dark.

Since the pressure effect is of such large magnitude as noted, we may conclude (from the constant value of $\alpha' \cdot i$) with some certainty that the

[1] Brown and Stebbins, PHYS. REV., Vol. 26, p. 273, 1908; PHYS. REV., N. S., Vol. 4, p. 85, 1914.

[2] *Loc. cit.*, article above.

Pressure.	Conductivity in Dark Ohms^{-1}.	Conductivity in Light Ohms^{-1}.	Recovery in .02 Sec. Change of Conductivity. $i = K \cdot N$	$a' = \frac{\Delta i}{i^2 \cdot \Delta t}$	$a' \cdot i$
P_1	1.79×10^{-7}	5.18×10^{-7}	1.84×10^{-7}	3.5×10^{7}	17.9
P_2	$6.50 \times$ "	$15.4 \times$ "	$4.12 \times$ "	$1.35 \times$ "	17.1
P_3	$12.2 \times$ "	$30.3 \times$ "	$9.02 \times$ "	0.445	14.2
P_4	$18.9 \times$ "	$43.9 \times$ "	$14.36 \times$ "	0.300	15.0
P_5	$23.8 \times$ "	$55.5 \times$ "	$15.5 \times$ "	0.26	14.0

coefficient of recombination varies inversely as the initial conductivity in the light, that results from the pressure.

Now it may be observed in the same table of data that the light sensitiveness at the different pressures is almost proportional to the conductivity in the dark accompanying each pressure. If, in equation (5), the value of q were small compared with M, it would be necessary for M (the rate of production by a fixed illumination) to vary directly with the initial conductivity at any pressure in order that this increase of light sensitiveness might be proportional to the dark conductivity.

We have, therefore, proved that the coefficient of recombination varies inversely as the conductivity ensuing from the pressure, and the evidence just stated inclines very much toward the view that the rate of production by light varies directly as the same conductivity resulting from the pressure effect.

General Considerations.

The attempt has been made to build up a simple electron theory to correlate the most fundamental photo-electro-mechanical properties in metallic selenium. The experiments have been carefully selected to verify the basic conceptions with a minimum number of postulates, by avoiding all questions of absorption, reflection and time rate of change of conductivity.

The effort has been successful in achieving a simple consistency of results. It was first shown that the electrons do recombine very rapidly with what is supposed to be the atomic structures, and the recombination takes place according to the same law governing the recombination of ions in gases. But we can not conclude from this that the current is transported in the same way in selenium as an ionization current in gases.

The basis of the theory receives further support in that a common explanation accounts both for the variation from Ohm's law and for the large changes of conductivity accompanying pressure changes. In each case the coefficient of recombination of the electrons is found to vary inversely as the variable conductivity imposed by the pressure change or the difference of potential. And likewise, there is common evidence that the rate of production of conducting electrons by a fixed illumination is

directly proportional to the variable conductivity imposed by pressure or voltage.

The temporary liberation of electrons by light bears certain resemblance to the original suggestion of Pfund[1] in which he compared light-action in selenium to an internal photo-electrical effect. This idea also is consistent with the experiments of Dr. L. P. Sieg and the author[2] where we have found all isolated crystals of selenium to have a maximum sensibility in the ultra-violet region of the spectrum.

But the experiments indicate a distinctly new idea as involved in a coefficient of recombination of the electrons that varies with the physical conditions surrounding the crystal, and also a varying rate of production of electrons with a fixed light intensity. This varying rate of freeing of electrons is governed by the same law apparently as that governing the variation of the recombination constant, except that the two relations are in inverse direction.

The form of the electron theory as here presented offers a satisfactory explanation of the electro-dynamical, light-electrical and electrical relations recently published.[3] The action due to pressure is not transmitted beyond the region of stress. The pressure merely lowers the stability of the selenium such that a given light intensity may liberate a greater number of electrons where this stress exists and such that the electrons recombine less rapidly in the same region.

Consistent with this interpretation, the light action transmitted to a distance is increased if the pressure is applied to the portion of the crystal where the conduction takes place, but the transmitted effect is not increased by pressure applied only at the place of illumination. The transmitted light action is of the nature of a crystal disturbance, which lowers the stability of the electrons everywhere in the confines of the crystal.

Since the analysis has shown the voltage effect to be identical with the pressure effect so far as the rate of recombination of electrons or their liberation is concerned, it is to be expected that the voltage effect could not be transmitted throughout the crystal in the way that light action is transmitted. This, in fact, is the result found in the previous work.[4]

Naturally the theory suggests many other lines of investigation in order to obtain more detailed information as to the nature of electric conduction in selenium. Since we have already considered such a wide range of experiments and have obtained such satisfactory agreement, the theory is one of unusual promise.

[1] PHYS. REV., Vol. 28, p. 234, 1909.

[2] PHYS. REV., Vol. 4, p. 48, and p. 507, 1914.

[3] PHYS. REV., N. S., 1914.

[4] *Loc. cit.*