The effect of temperature on the resistance, the rate of recovery, and the light-sensibility of certain selenium crystals

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THE EFFECT OF TEMPERATURE

on

THE RESISTANCE, THE RATE OF RECOVERY, AND THE LIGHT-SENSIBILITY

of

CERTAIN SELENIUM CRYSTALS.

by

Kathryn Johnstone Dieterich.

A thesis

submitted to the faculty of

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Master of Science.

June 16, 1915.
The Effect of Temperature on the Resistance, the Rate of Recovery, and the Light-sensitiveness of Certain Selenium Crystals.

In this paper an attempt will be made to show the influence of temperature upon the rate of recovery, upon the light and dark resistance, and upon the sensitiveness to light action of certain crystals of metallic selenium.

The general method of procedure, at each temperature, was to measure the equilibrium resistance, in the dark, the equilibrium resistance in the light, and the resistance a few hundredths of a second after the light had been cut off from the crystal. All other conditions, such as pressure, voltage, light intensity, and time of recovery, were kept constant.

APPARATUS

The apparatus used in carrying out the experimentation is shown diagrammatically in Fig. 1. The crystal (C) to be investigated was mounted between metal electrodes (E), and placed in one arm of a Wheatstone bridge circuit. A constant voltage was maintained over the crystal by means of storage batteries (B). The pressure on the selenium was kept constant by means of a weight of 75 gr. suspended from the upper electrode and insulated from the lower. The electrode and crystal were kept in a light-proof, self-regulating electric oven, so that the temperature might be varied. The exact temperatures were determined by means of a galvonometer in series with a thermo-couple of constantan and copper wires, one junction (X1) being close
to the crystal, the other ($X_2$) outside the oven. The junction ($X_2$) was kept at 0°C. by means of ice and water.

The source of illumination was a Nernst glower ($N$) at a distance of 45 cm., the light from which was focussed on the crystal by a lens ($L$). The intensity of the light was kept constant by maintaining over the lamp a voltage of 115 v. from storage batteries.

The equilibrium values of the resistance of the crystal in the light and in the dark were measured in the usual manner by the Wheatstone bridge method. In order to measure the resistance after the light was cut off for .02 sec., the method of Brown and Clark was used, viz; a timing pendulum, in series with the galvonometer ($G$) was fitted with keys ($K_1$ and $K_2$) and arranged to operate a metal shutter, which moved between the crystal and the source of light, thus shutting off the illumination for a given period.

The crystal was allowed to come to equilibrium in the light, and then its resistance was measured. At this time the pendulum was in the position $P_1$, and both keys were closed. $K_2$ was now opened, breaking the circuit through the galvonometer. The pendulum was then released, striking $K_2$, and putting the galvonometer in circuit at the same instant the shutter cut off the light from the crystal. Just .02 sec. later the pendulum opened $K_2$, breaking the galvonometer circuit. During the .02 sec. it was in circuit, the galvonometer showed a deflection due to a change of resistance in the crystal from which the light had been removed. The actual change of resistance which corresponds to this deflection was later determined by substituting for the crystal a carbon resistance, which

could be adjusted until upon tripping the pendulum the same galvonometer deflection was obtained as was given by the crystal. This resistance could then be measured by the usual Wheatstone bridge method, and was equal to the resistance of the crystal after .02 sec. recovery.

The temperatures above room temperature were obtained by means of the electric oven; those below by surrounding the crystal with ice, ice and salt, CO$_2$ snow, or liquid air. The apparatus used for the cold temperatures was so constructed that it could be removed, filled and returned without touching or jarring the crystal. Two views of it are shown in Fig. 2. C is the crystal, between the electrodes E, surrounded by the tin box, in which BB is the compartment for holding the cooling substance, and G is a glass plate to permit light to fall on the crystal.

Fig. 2.
THEORETICAL

When a crystal of metallic selenium has been exposed to light, and the light is suddenly removed, the conductivity of the crystal does not return instantly to the value of equilibrium dark conductivity, but decreases rapidly at first, then more slowly, requiring several minutes, and even hours, to attain its true value, depending on the temperature. When a gas is exposed to a source of ionization, and the source is suddenly removed, the conductivity decreases rapidly at first, then more slowly, until equilibrium is restored. In gases the decrease in conductivity during the first short interval of time is ascribed to the recombination of the conducting electrons with the positive residues. It has been shown by Rutherford, 1), McClung 2), McClelland 3), and more recently Plimpton 4), that if there are present $n_1$ negative ions and $n_2$ positive ions the rate of recombination is directly proportional to $n_1 \times n_2$, that is:

$$\frac{dN}{dt} = -\alpha n_1 n_2$$

where $\alpha$ is a constant and is called the coefficient of recombination.


In order to study the effects of pressure, light intensity, and electromotive force on the rate of recovery of selenium, in cells and in crystals, Professor Brown assumes that for the first short interval of time after the light has been removed the decrease in conductivity of a selenium cell or crystal is due to the recombination of the conducting electrons with positive residues, and that this recombination takes place according to the same law as that which holds for gases. If the number of electrons taking part in the conduction is proportional to the conductivity, then the rate of recombination may be calculated from the formula:

\[ \alpha_1 = \frac{\Delta C}{C^2 \Delta t} \]

where \( \Delta C \) is the decrease in conductivity during the time \( (\Delta t) \) that the crystal has been in the dark, \( C \) is the equilibrium value of the conductivity in the light, and \( \alpha_1 \) is proportional to the coefficient of recombination. In order to obtain this result Professor Brown found it necessary to make the following assumptions:

1. When a crystal is in equilibrium in the light of dark the conductivity is proportional to the number of negative electrons taking part in the conduction.

2. Recombination takes place according to the same law as in gases.

2). Loc. cit.
3. The rate of recombination is the same in the light as in the dark.

The above conception was verified, approximately, by varying the conductivity over a wide range. This was done by changing the intensity of the illumination. Since the rate of recombination was found to be nearly proportional to the square of the conductivity, it was assumed that the recombination followed the same law as in gases.

In this paper the results of an investigation of the effect of temperature on the rate of recovery of selenium crystals will include a discussion of the effect of temperature upon the coefficient of recombination, calculated according to the above theory.
RATE OF RECOVERY

The crystals used were prepared by Dr. Brown as described by him. They were of three kinds: the large hexagonal, the needle-shaped acicular, and the monoclinic lamellar. In each case the current was passed through the crystal in a direction perpendicular to the long axis, and the crystal illuminated in a direction perpendicular to the direction of the current.

In general the coefficient of recombination was found to decrease with increase in temperature.

Table 1.

<table>
<thead>
<tr>
<th>Temperature in °C.</th>
<th>Temperature in °Abs.</th>
<th>Conductivity in light Ohms $\times 10^{-7}$</th>
<th>$\alpha \times 10^{-7}$</th>
<th>$\alpha \times C$</th>
</tr>
</thead>
<tbody>
<tr>
<td>-89</td>
<td>184</td>
<td>1.685</td>
<td>3.640</td>
<td>6.11</td>
</tr>
<tr>
<td>-68</td>
<td>205</td>
<td>2.057</td>
<td>3.28</td>
<td>6.75</td>
</tr>
<tr>
<td>-40</td>
<td>233</td>
<td>3.58</td>
<td>1.68</td>
<td>6.02</td>
</tr>
<tr>
<td>0</td>
<td>273</td>
<td>7.07</td>
<td>0.875</td>
<td>6.17</td>
</tr>
<tr>
<td>19</td>
<td>292</td>
<td>7.46</td>
<td>0.835</td>
<td>6.22</td>
</tr>
<tr>
<td>21</td>
<td>294</td>
<td>7.88</td>
<td>0.754</td>
<td>5.93</td>
</tr>
<tr>
<td>26</td>
<td>299</td>
<td>8.07</td>
<td>0.73</td>
<td>5.89</td>
</tr>
<tr>
<td>33</td>
<td>306</td>
<td>8.66</td>
<td>0.606</td>
<td>5.23</td>
</tr>
<tr>
<td>43.5</td>
<td>316.5</td>
<td>9.07</td>
<td>0.548</td>
<td>4.95</td>
</tr>
<tr>
<td>56</td>
<td>329</td>
<td>9.31</td>
<td>0.537</td>
<td>4.99</td>
</tr>
<tr>
<td>64</td>
<td>337</td>
<td>5.89</td>
<td>0.367</td>
<td>2.17</td>
</tr>
<tr>
<td>75</td>
<td>348</td>
<td>8.32</td>
<td>0.316</td>
<td>2.62</td>
</tr>
</tbody>
</table>

Table 1. shows the results obtained with hexagonal crystal No.2. There is seen to be a large fall in the value of $\alpha$ with increase of temperature from -69°C. to about 0°C. after which

Crystal No. 2.

Fig. 3.
the decrease is more gradual to 75°C., which is as high a temperature as could be reached. It was often necessary to maintain these temperatures for several hours in order that steady conditions might be reached. After a temperature of 50°C. or more had been kept for longer than an hour the conductivity of the crystal began to decrease materially. This was at first ascribed to slow oxidation of the brass electrodes, and was no doubt partly due to this cause. However when nickel or platinum electrodes were substituted the same effect to a less extent was observed. Upon examining the electrodes it was discovered early in the experimentation that a dark deposit was formed just where the crystal touched each the upper and lower electrodes. This could be removed with a piece of fine emery paper, and the crystal resumed its former resistance until more deposit formed. The effect of this deposit was to depress both the values of conductivity and of \( \alpha \), so that the last two points in the curve (Fig. 3) are only approximately correct.

Crystal No.13 (Table 2) shows in general the same result: a large decrease of \( \alpha \) with increased temperature. In these measurements platinum electrodes were used, and the temperature was not high enough to produce sufficient deposit to cause any appreciable error.
Crystall No. 13.
Table 2.

<table>
<thead>
<tr>
<th>Crystal No. 13</th>
<th>E.M.F. = 6 volts.</th>
<th>Pressure = 76 gr.</th>
</tr>
</thead>
<tbody>
<tr>
<td>Temperature in °C.</td>
<td>Temperature in °Abs.</td>
<td>Conductivity in light7 Ohms x10</td>
</tr>
<tr>
<td>-40</td>
<td>233</td>
<td>2.63</td>
</tr>
<tr>
<td>- 7</td>
<td>266</td>
<td>4.35</td>
</tr>
<tr>
<td>10</td>
<td>283</td>
<td>7.10</td>
</tr>
<tr>
<td>21</td>
<td>294</td>
<td>6.05</td>
</tr>
<tr>
<td>32</td>
<td>305</td>
<td>6.82</td>
</tr>
<tr>
<td>41</td>
<td>314</td>
<td>7.38</td>
</tr>
</tbody>
</table>

The curve, Fig.4, shows a slight depression in α at 10°C which may, or may not be a genuine effect. However, two complete series of readings gave a low value of α at just this temperature. It may be of interest to mention here that although a crystal had been removed from the electrode for several weeks it could be returned and, if the previous conditions as to light intensity, pressure, and voltage were restored, the same curve of α and temperature, giving the same values of α as before.

Other crystals showed essentially the same change of α with temperature. In some cases there were depressions, as in No. 13; one crystal, No. 3, a lamellar type, showed quite a sharp kink at about 35°C.

Thus, each of the three types of crystals showed the same effect of temperature on the coefficient of recombination: a general decrease of α with increase of temperature.
Fig. 5.

Plotted from Erikson's data, Phil. Mag., 18, p. 335, 1909.
H. A. Erikson[^1], in 1909, made a determination of the effect of temperature upon the coefficient of recombination in gases. He obtained a curve showing the relation between $\alpha$ and $T$, which resembles very closely the curve obtained for crystal No. 2, (Fig. 3). His curve is shown in Fig. 5. What significance there is, if any, in this striking similarity is not yet evident.

If then, the recovery of selenium crystals is due to a recombination of negative electrons with positive residues and the rate of recombination is expressed by the formula

$$\frac{\Delta \alpha}{\Delta t} = \alpha C^2,$$

the coefficient of recombination $\alpha$, varies with temperature.

It will be noticed in tables 1 and 2 that, while the coefficient of recombination is not a constant at all temperatures, the product $\alpha \times C$, is very nearly so. A glance at the curves, Figs. 3, 4, and 5, will show that this relation suggests itself here also; since, wherever a rise occurs, in the $\alpha$-curve a depression appears in the $C$-curve. The same general relation between the shape of the $\alpha$-curve and the $C$-curve is apparent in Erikson's work with gases. Dr. Brown[^2] has found that $\alpha \times C$ is a constant for selenium crystals when pressure or voltage varied the conductivity, although $\alpha$ is not constant.

Since $\alpha \times C$ is a constant and is equal to $\Delta C/C \times \Delta t$, the rate of recovery during the first short interval of time is

equal to some constant, \( \beta \), times the conductivity in the light. 

\[ \frac{\Delta C}{\Delta t} = \alpha C^2 = \beta \cdot C, \]

where \( \beta \) is equal to \( \alpha \cdot C \), and we have the simple relation that the rate of recovery of selenium crystals is proportional to the conductivity in the light. This proportionality did not appear to hold with much accuracy at the higher temperatures. For the large range of temperatures over which it does hold, however, the rate of recovery may be said to be independent of temperature, pressure, and voltage.
16.

RESISTANCE.

Conductivity is determined by taking the reciprocal of the resistance, so that a study of the effect of increase of temperature upon the conductivity of selenium crystals should give an adequate idea of its effect on their resistance. In crystal No. 2, Fig. 3, it will be seen that the conductivity in the light at low temperatures was small, increased with increasing temperature and passed through a maximum in the region of 55°C. The fall of conductivity above 55°C might have been influenced by oxidation of the brass electrodes which were used with crystal, so that the apparent decrease was somewhat exaggerated. Crystal No. 13, Fig. 4, showed a general increase of conductivity in the light with increased temperature. There was, however, a decrease for a short interval from 10°C to 21°C after which the conductivity rose again as the temperature increased. Depressions of this kind were found in the C-curves of many of the crystals, although not always at this same temperature. One crystal, No. 4, had a sharp depression and sudden rise in the region of 0°C. Ries\(^1\) found the same condition to hold for selenium cells, with the minimum most often around 100°C, but that he was able to shift the position of this minimum to below 0°C by certain heat treatment. The general tendency, however, in cells and crystals is for an increase of conductivity, and a consequent decrease of resistance, to result from an increase of temperature.

\(^1\) Die elektrischen Eigenschaften und die Bedeutung des Selens für die Electrotechnik, 1908.
Fig. 6.

○ --- Crystal No. 2.
○ --- Crystal No. 13.

\[ \frac{\kappa}{10^7} \]

T, in °Abs.

Fig. 6.
The equilibrium dark conductivity will be seen from the curves in Fig. 6 to follow much the same general tendency: an increase of conductivity with increase of temperature. The same maximum and minimum which was found in the light conductivity curves is apparent here.
LIGHT SENSITIVENESS.

The light sensitiveness of a selenium crystal may be expressed as:

1. The ratio of the change of resistance to the resistance in the dark. That is, the difference between the resistance in the dark and in the light divided by the resistance in the dark.

2. The rate of production of conducting electrons by the light.

In the former case the sensibility may be expressed as a function of the conductivities, since they are more easily worked with than the resistances. The sensibility, "S", then becomes:

\[
S = \frac{\Delta R}{R_d} = \frac{R_d - R_1}{R_d} = \frac{1/C_d - 1/C_1}{1/C_1} = \frac{C_1 - C_d}{C_1}
\]

where \( R_d \) and \( C_d \) are the resistance and conductivity in the dark, and \( R_1 \) and \( C_1 \) the resistance and conductivity in the light. When sensitiveness calculated thus was plotted with absolute temperature, Fig. 7, the sensitiveness, in general, decreases with increase of temperature, at first slowly, then more rapidly, although the change in sensibility over a fairly large range of temperature was not great.

If the sensibility was measured as the rate of production of conducting electrons by the light, the curves in Fig. 8 result. Dr. Brown\(^1\) has shown how this rate of production may be calculated.

1). Loc. cit.
O -- Crystal No. 2.

@ -- Crystal No. 13.

Fig. 7.

Fig. 8.

$T$, in °Abs.

T, in °Abs.
\[ \frac{dC}{dt} = M + q ; \]

where \( \frac{dC}{dt} \) is the rate of production of electrons when the crystal is in equilibrium in the light; \( q \) is the rate of production of electrons in the dark, and \( M \) is the rate of production by the light. \( \frac{dC}{dt} \) must also be equal to the rate of recombination, \( \alpha C^2 \), since the crystal is in equilibrium. For the first few hundredths of a second after the illumination is removed

\[ \frac{dC}{dt} = \alpha C^2 = M + q \]

When the crystal is in equilibrium in the dark, the rate of production of electrons, \( q \), is equal to the rate of recombination, \( \alpha C_d^2 \), and \( M \) is zero. When the crystal is in equilibrium in the light,

\[ \frac{\Delta C}{\Delta t} = M + \alpha C_d^2 \]

\[ M = \frac{\Delta C}{\Delta t} - \alpha C_d^2 \]

\[ = \alpha C_1^2 - \alpha C_d^2 \]

It is shown, Fig. 8, that sensibility calculated in this way gives a different curve with temperature than when calculated according to the first case. Here the sensibility increases with increased temperature.

These two methods of representing sensibility cannot, then, be expressions of the same phenomenon. The sensibility may be thought of as the measure of the light effect on the crystal.
If, by this effect, is meant the rapidity with which the crystal responds to light, we may use as our definition of sensibility the rate of production of electrons by the light, $M$, and this rate does increase with rise of temperature as the curves in Fig. 8 show. But if the total effect of the light is meant, sensibility must be expressed as $\Delta R/R_d$, and this ratio decreases as the temperature increases, as is shown by the curves in Fig. 7.
SUMMARY.

In conclusion, it may be said in regard to the effect of temperature on certain properties of selenium crystals, that,

1. The resistance, in the dark and in the light, is, in general, decreased by increase of temperature, with a small increase in some cases in the region 0°C to 50°C.

2. The coefficient of recombination, $\alpha$, calculated according to the formula,

$$\alpha = \frac{\Delta C}{C_1 \Delta t}$$

is not constant at all temperatures, but decreases with increase of temperature in much the same manner that the coefficient of recombination in gases decreases with increase of temperature.

3. Over a wide range of temperature the rate of recovery for the first few hundredths of a second is proportional to the conductivity in the light.

$$\frac{\Delta C}{\Delta t} = -\beta \cdot C_1$$

4. The sensitiveness to light does not vary greatly over a wide range of temperatures until the region of 50°C is reached, when it begins to decrease rapidly.

I wish to acknowledge my indebtedness to the staff of the Department of Physics for their interest in the problem, and especially to Dr. Brown for suggesting it, and for his encouragement during the progress of the work.