



LIII. On the variation of resistance of selenium with temperature

Snehamoy Datta M.Sc. D.I.C.

To cite this article: Snehamoy Datta M.Sc. D.I.C. (1921) LIII. On the variation of resistance of selenium with temperature , Philosophical Magazine Series 6, 42:249, 463-470, DOI: [10.1080/14786442108633784](https://doi.org/10.1080/14786442108633784)

To link to this article: <http://dx.doi.org/10.1080/14786442108633784>



Published online: 08 Apr 2009.



Submit your article to this journal [↗](#)



Article views: 2



View related articles [↗](#)



Citing articles: 3 View citing articles [↗](#)

LIII. *On the Variation of Resistance of Selenium with Temperature.* By SNEHAMOY DATTA, M.Sc., D.I.C., Research Student, Imperial College of Science and Technology*.

1. *Introductory.*

THOUGH the light sensitiveness of selenium has been very well studied by a large number of workers, it seems rather surprising that the corresponding heat sensitiveness has been studied by only two observers †, whose results appear to differ from one another considerably. It was therefore thought worth while to measure the temperature coefficient of electrical resistance of selenium, with a view to decide the more important question—viz., how far the special properties of selenium are attributable to the changes in conductivity caused by changes in temperature. The results of the experiments have given rise to some suggestions, which have also been discussed here.

2. *Experiments and Observations.*

Several cells were prepared by pressing melted amorphous selenium between two glass plates about 1 sq. in. in size and having a thickness of about .025 in. Two copper electrodes and one junction of a copper-constantan thermo-couple were imbedded in selenium before it was annealed. The process of annealing was carried out with the cell in a light-tight enclosure, and usually consisted in keeping the cell at about 200° C. for nearly five minutes and subsequently lowering its temperature to about 170° C. It was kept at this temperature until the cell reached its maximum conductivity. This was determined by putting the cell in series with a battery and a galvanometer while annealing. At first no deflexion was observed—presumably the selenium was in the non-conducting state. In about half an hour slight conductivity was noticed; from then onward, deflexions of the galvanometer were observed every five minutes, showing a gradual increase in conductivity, at first slowly and then rapidly. After about three hours the rate of increase in conductivity appeared to be very slow, and subsequently a very slow decrease was noticed. In most cases at this stage the annealed selenium was allowed to cool suddenly. On two occasions, however, annealing was further continued,

* Communicated by Prof. A. O. Rankine, D.Sc.

† S. Bidwell, *Phil. Mag.* vol. xv. p. 31; C. Ries, *Phys. Zeit.* vol. ix. p. 228 (1908).

with the result that the resistance of the cell gradually but unsteadily increased. The unsteadiness may be due to small fluctuations, usually 2 to 3 degrees, in the temperature of the electric heater used for the purpose of annealing. The cell being maintained at about 170°C . overnight, was found next morning to have increased its resistance considerably.

For the experiment on the variation of resistance with temperature, the selenium cell under test was enclosed in a light-tight double-walled copper vessel whose temperature could be controlled within half a degree by regulating the heating current. The cell formed part of a circuit consisting of a 4-volt accumulator and a calibrated galvanometer, a key being inserted to complete the circuit at will. The temperature of the cell was determined by the thermocouple, which formed part of the circuit of a second calibrated galvanometer. Though this method is less accurate than the potentiometer method, it was more convenient, and gave results accurate to about $1/10$ of a degree centigrade.

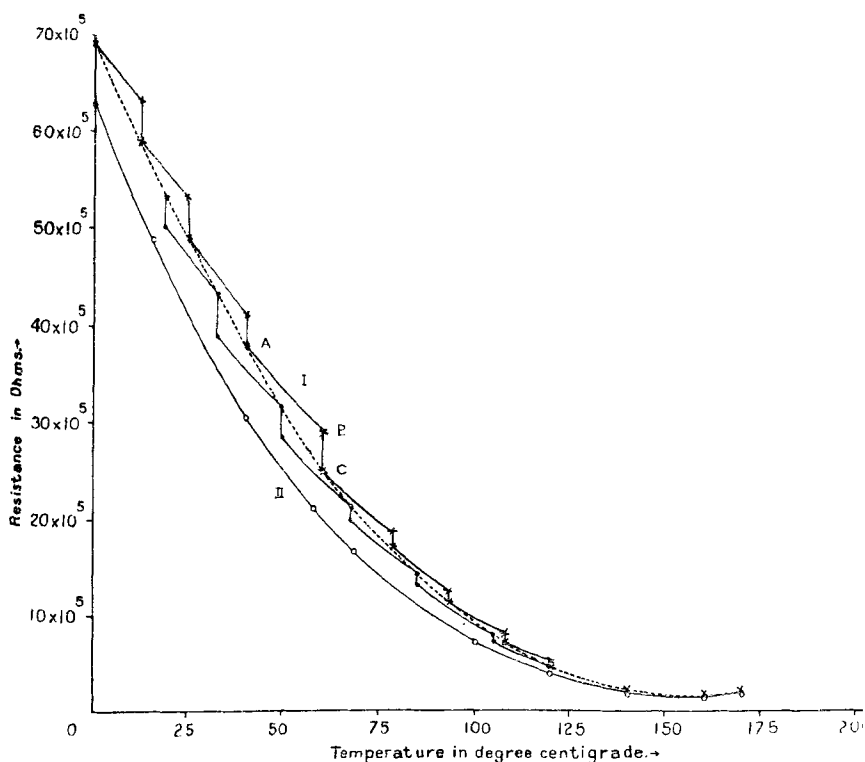
In spite of the reputation selenium cells commonly have of being subject to unaccountable variations, those used in this investigation were found to be reliable, and the effect of heat on them was quantitatively reproducible again and again. But this required certain precautions to be taken, which will be clear in the light of the following observations. In the course of this experiment, which has been repeated over twenty times, there were definite indications that the change in resistance is intimately connected with the time taken in producing the variation in temperature. Not only does it depend on the rate of heating or cooling, as the case may be, but the future behaviour of the cell depends very much upon the period during which it is kept at a fixed temperature before being subjected to a variation in temperature. If a selenium cell after being annealed is brought down to room temperature and maintained at that temperature for a considerable time, and then subjected to a change in temperature, the change in resistance is much less than when the cell is immediately brought down from a somewhat higher temperature. Or, in other words, the shape of the resistance temperature curve is less steep when the temperature is changed after a long period of constant temperature. And this has been noticed, not at room temperature alone, but at all temperatures up to about 120°C . It seems as if, after long being maintained at a constant temperature, the selenium is sluggish in changing its physical properties connected with a variation in temperature. Hence, to get reproducible results, it is very important

that the experiment should be repeated in all its details in exactly the same way, with the same rate of variation of temperature. It is clear that in order to be sure that the thermo-couple records truly the temperature of the whole of the selenium, changes of temperature, whether heating or cooling, must be arranged to take place sufficiently slowly. This precaution has been taken, with the result that the cooling curves show satisfactory agreement with the heating curves.

3. Results.

In each case the resistance observed was plotted against the temperature; and for the several cells of the same dimensions examined, although they differed considerably in their initial resistance, the form of the curve was the same, and at

Fig. 1.



temperatures higher than about 130° C. the different curves very nearly coincided with one another. Two typical cases are shown in fig. 1. Curve I. shows the effect of time in

Phil. Mag. S. 6. Vol. 42. No. 249. Sept. 1921. 21

reducing the resistance; the portion of the curve parallel to the ordinate marks the change in resistance obtained by keeping the cell at a fixed temperature till no further change in resistance is observed*. The dotted curve thus shows the ultimate resistances appropriate to various temperatures. Curve II. is obtained with a different cell by changing its temperature exceedingly slowly, so as not to show any resistance lag, the discontinuities in curve I. being now absent. The form of the curve suggests that the variation of resistance with temperature is expressible by an empirical equation of the ordinary type:

$$R_t = R_0 + bt + ct^2.$$

The constants b and c are not general constants for selenium, but depend on the annealing and the past history of the cell. The values of b and c , having been derived by the solutions of equation supplied by the experimental data, Table I. shows the agreement between the experimental data and those calculated from the equation:

$$R_t = [65.01 \times 0.86t + .0029t^2] 10^5.$$

TABLE I.

Temp. in deg. centigrade.	R (obs.) in ohms.	R (cal.) in ohms.
0.0	66.0×10^5	65.01×10^5
3.3	62.2	62.20
6.5	59.1	59.54
13.0	54.6	54.32
20.0	49.1	48.97
40.0	34.6	35.24
60.0	23.8	23.84
78.0	15.4	15.57
87.0	11.9	12.14
100.0	8.0	8.10
120.0	3.5	3.52
137.0	1.9	1.62
160.0	1.7	1.64
170.0	2.0	2.62

As shown in the curves, whatever may be the initial resistances of the cells, their resistances (for cells of the same dimensions) beyond 130°C. very nearly coincide, and

* The time allotted for making the change of temperature, *e. g.* from A to B, was about 10 minutes. The subsequent time necessary before the resistance became constant at C was of the order of 25 minutes, showing that the process is a deliberate one not attributable to failure of the thermo-couple to record the true temperature.

the total change of resistance from 130° C. to 170° C. is about $1/30$ of that from 0° C. to 130° C. It is also remarkable that beyond 130° C. all time lags, as well as the light and voltage effects, disappear.

Several experiments were made to find out the resistance between 170° C. to 217° C. (melting point), but no definite conclusions could be arrived from them. Beyond 170° C., selenium begins to sublime, so that the results obtained cannot be taken as trustworthy; but in almost all the cases the cells showed a decrease in conductivity. Whether this is due to a partial transformation into the amorphous variety or a true increase in resistance, could not be definitely ascertained*. It is, however, striking that the calculated values also increase beyond 170° C.

4. Discussion of Results.

The results of the present experiment are thus in serious contradiction to the results obtained by previous observers; for S. Bidwell†, who made a similar set of experiments, has found that "when the temperature of the cell reaches a point which is in general a few degrees higher than the average temperature of the air, a maximum resistance is obtained; and if the heating is continued, the resistance begins to decrease." As is well shown by the curve, not the slightest tendency is noticed of any increase in resistance between 0° C. and 170° C. It is, however, not clear from his paper whether he experienced the influence of "time" previously described and took the necessary precautions.

S. Bidwell used his results in an attempt to refute Dr. Moser's view‡ that the light sensitiveness is perhaps due to the heating caused by light. The result of the present experiment therefore reopens the question.

A separate experiment was therefore made to test how far the heating of the selenium due to light is responsible for the light sensitiveness. One of those cells whose temperature coefficient had been previously determined was therefore enclosed in a light-tight box provided with a photographic shutter, the whole being placed in a Dewar's flask, which forms the simplest heat insulator. First of all, the selenium circuit was made for a few seconds, with the selenium in the dark, in order to determine the dark current. The shutter

* It may be a transformation into the β modification of Ries (*loc. cit.*), which shows an increase of resistance with temperature.

† S. Bidwell, *loc. cit.*

‡ Moser, *Phil. Mag.* (5) vol. xii. p. 212.

was then opened, exposing the selenium to visible rays alone, the infra-red and ultra-violet rays being cut off by a thick glass plate. The thermo-couple indicated a slight increase in temperature (about 1 degree). The results obtained are given below:—

TABLE II.

Resistance in dark	67.0×10^5 ohms.
Resistance in light	48.0×10^5 „
Change in resistance	19.0×10^5 „

Comparing the decrease in resistance (7.5×10^5) due to a rise in temperature of about one degree with the total decrease in resistance (19.0×10^5) observed on exposure to light, it was found that not more than $1/25$ of the total decrease could be attributed to the heating due to light. The light-effect is thus a genuine one independent of the heat-effect.

As has been pointed out before, time plays a great part in moulding the future behaviour of the cell. And this is not peculiar to the variation of resistance with temperature alone, for it is well known that the light sensitivity of selenium, particularly the recovery curve, largely depends on the time of exposure. The voltage effect, too, depends to a great extent on the time of application of the voltage. It seems difficult to realize fully the part played by time on any theory—electronic in nature—which has been propounded to account for the many peculiar properties of selenium. It can, however, be best understood if the old theory*, viz. transformation into some other allotropic forms, be a little modified. Instead of assuming that the transformation from one modification to another takes place at one definite temperature, it may be supposed that the transformation takes place at all temperatures. The various modifications may be regarded as maintaining a sort of dynamic equilibrium amongst themselves, the quantity of each variety depending on the particular temperature—the lower the temperature the more the amount of the less conducting variety—and the degree of stability of each

* In this connexion it is well to recall the observations of R. Marc (*Die physikalische-chemischen Eigenschaften des metallischen Selen.* L. Voss, Leipzig, 1907), who, by the investigation of the heat changes, the electrical conductivity, and the microscopic investigation of the surface, was able to detect with certainty the existence of two polymorphic forms. The one form was crystallized by heating the selenium at a temperature of about 100°C. , and was essentially non-conducting. At a temperature of about 200°C. this form passed to the conducting variety.

modification depending on the time during which it is maintained at one temperature. So that with a change in temperature there is a change in the quantity of the various modifications, the equilibrium stage being arrived at very slowly *. After this, if the temperature is allowed to remain constant, the degree of stability of each variety increases or the velocity of further transformation decreases, and it becomes more and more sluggish to change that condition. That this is perhaps the actual case, may be realized from the fact that a cell, maintained for a long time at one temperature and subsequently subjected to a small change of temperature, requires a very long time to assume its ultimate conductivity appropriate to that temperature—much longer, for example, than in the experiments to which fig. 1 refers.

5. Observations with Selenium Crystals.

The conclusions drawn from the above experiments being well supported by the modified theory of transformation, and it being well known that the process of annealing is nothing but a crystallization of the amorphous variety, it was hoped to repeat the experiments with crystals produced by the condensation of molten selenium at various temperatures. The method suggested by Brown† was adopted, but as the crystals so formed were not large enough to test them individually, no quantitative experiment was pursued. Of those mentioned by Brown, three different varieties of crystals were recognized :—

- (1) Needle-shaped crystals.
- (2) Groups of white acicular crystals.
- (3) Groups of reddish acicular crystals.

Of these, the first variety showed a striking behaviour. Several of these formed a network and were deposited on the wall of the tube. They appeared red in the reflected light and greyish black in the transmitted light, and had a moderate conductivity at room temperature. On slightly

* The velocity of such transformations is very slow, particularly at low temperature. But Berger (*Zeitschrift für Anorganische Chemie*, vol. lxxxv. p. 75 (1914), has shown that by the presence of certain catalytic agents as silver selenide, the rate of transformation is greatly increased. This therefore indirectly supports the theory of transformation. The influence of the catalytic agent in increasing the velocity of transformation may eventually explain the more marked effect near the electrodes, as observed by S. Bidwell (*Chemical News*, vol. lii. p. 191) and more recently by White (*Phil. Mag* (6) vol. xxvii. p. 370).

† Brown, *Phys. Rev.* vol. iv. p. 85 (1914).

warming them up, the reddish colour gradually disappeared with a simultaneous increase in conductivity. On allowing them to cool, they very slowly began to present the former tint, conductivity, too, decreasing at the same time. The second variety of crystals were usually found to be deposited in the hotter part of the tube, and had slight conductivity which did not show any appreciable change on slightly heating. The third variety was primarily non-conducting. The peculiar heat sensitivity of the first variety is therefore quite possibly responsible for the enormous temperature variation of resistance of selenium; and that something akin to transformation is actually taking place, is suggested from the change of colour on warming. It is hoped that, time being available, researches will be pursued in this direction.

6. *Summary.*

1. The variation of resistance of selenium with temperature has been carefully determined, and a formula has been proposed to express the said variation.

2. It has been shown experimentally that not more than $1/25$ of the "light effect" is attributable to heat produced by light.

3. A change of colour taking place at the same time as the change in resistance has been observed by warming crystals of selenium produced by the sublimation method.

4. A modified theory of transformation is suggested to account for the various observations in connexion with the heat-effect.

In conclusion, I beg to thank Prof. A. O. Rankine for the kind interest he took in this work and for the facilities given to me in conducting the experiment.

LIV. *The Effect of Gravitation on Light.*

By HAROLD JEFFREYS, M.A., D.Sc.*

THE query in Sir Oliver Lodge's note (Phil. Mag., June 1921, pp. 944-5) concerning the legitimacy of deriving the equations

$$\gamma \frac{dt}{ds} = k \quad \text{and} \quad r^2 \frac{d\theta}{ds} = h$$

for the motion of a light wave is relevant to my paper "On the Crucial Tests of Einstein's Theory of Gravitation." (Monthly Notices of R. A. S., Dec. 1919, pp. 138-154). Of

* Communicated by the Author.