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Prof. W. G. Adams, F. R. S. and Mr. R. E. Day.

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V. "The Action of Light on Selenium." By Prof. W. G. Adams, F.R.S., and Mr. R. E. Day. Received May 18, 1876.

(Abstract.)

The paper contains an account of a series of experiments which have been carried on during the past year, and which have had for their object the investigation of the electrical behaviour of selenium, especially as regards its sensitiveness to light. The first part contains a short summary of the results obtained by Professor Adams, which have been communicated to the Society *.

It has been already shown that the action is due principally, if not entirely, to those rays of the spectrum which are luminous, and that the ultra-red or the ultra-violet rays have little or no effect; also that the intensity of the action depends on the illuminating power of the light, being directly as the square root of that illuminating power.

It was also observed that with the same piece of selenium at the same temperature, the resistance diminished as the battery-power was increased. Also it was found that the electrical resistance of the rod of selenium was different for currents going through it in opposite directions. Thus if two platinum wires be melted into the selenium at two points, A and B, and the resistance of the selenium be balanced by the Wheatstone's bridge arrangement, the positive pole of the battery being connected to the electrode A, then on reversing the current so that the negative pole of the battery was now connected to the electrode A, the numerical value of the balancing resistance was always found to be different from that previously obtained.

If the electrical conductivity of selenium followed the ordinary law of metallic conduction this would not be the case; and hence it seemed probable that a careful investigation of these points would lead to some important results.

In the experiments recorded in this paper, the objects we have had especially in view have been:—

(i) To examine the character of the electrical conductivity of selenium when kept in the dark.

(ii) To determine whether light could actually generate an electric current in the selenium.

Several pieces of selenium were prepared as follows:—A small piece varying from a quarter of an inch to an inch in length was broken off a stick of vitreous selenium. A platinum wire was then taken and bent round into a small ring at one end, and the remainder of the wire turned up at right angles to the plane of this ring. The rings of two such wires were then heated in the flame of a spirit-lamp, and pressed into the ends of the little cylinder of selenium,

* See 'Proceedings,' vol. xxiii. p. 535, and vol. xxiv. p. 163.

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thus forming platinum electrodes. The whole was then annealed. After annealing copper wires were soldered on to the platinum electrodes, and the selenium was then inclosed in a piece of glass tube, the electrodes being passed through corks fixed at the ends of the tube. A numbered label was then attached to one of the electrodes, and this was then always described as the "marked" electrode.

The method of annealing which we have found to give the best results is very simple. A large iron ball is heated to a bright red heat, and then placed in a large iron bowl of sand; the sand is then heaped up all over the ball, and left for an hour. The ball is then taken out, and the selenium, wrapped up in paper, is put into the hot sand and left there for twenty-four hours. On removing it from the sand its appearance has generally changed from a bright glassy character to a dull slate-coloured one; and when this is the case its conductivity is generally very good.

In most of our experiments it was important to know what was the *direction* of the current in any particular case, and we therefore decided to call those currents direct or positive currents when the positive electrode of the battery was connected with the *marked* electrode of the selenium plate under examination. In order to be able to reverse the current with respect to the selenium without affecting any other portion of the circuit, the ends of the wire electrodes of the selenium were made to dip into two little mercury cups fixed on a plate of ebonite, and then were connected to the binding-screws of the Wheatstone bridge arrangement. Thus by reversing the position of the electrodes the direction of the current through the selenium was reversed. The positive direction of the current was always determined at the commencement of each series of experiments by means of a delicately suspended magnetic needle.

A few preliminary experiments were made to determine whether the change of resistance with change of direction of the current had any connexion with the position of the selenium or the direction of the current with respect to the magnetic meridian. No such connexion was found to exist.

From the results obtained from a great many experiments made to determine the diminution of resistance with increased battery-power, and the change of resistance with a change of the direction of the current, the following conclusions were drawn:—

(1) That on the whole there is a general diminution of resistance in the selenium as the battery-power is increased.

(2) The first current through the selenium, if a strong one, causes a permanent *set* of the molecules, in consequence of which the passage of the current through the selenium during the remainder of the experiments is more resisted in that direction than it is when passing in the opposite direction.

(3) The passage of the current in any direction produces a *set* of the

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molecules which facilitates the subsequent passage of a current in the opposite, but obstructs one in the same direction. Hence when two currents are sent through successively, after a very small interval, in the same direction, the resistance observed in the second case, even with the higher battery-power, is often equal to or greater than it was before.

The results of these experiments seeming to indicate that the conductivity of selenium is electrolytic, a number of experiments were undertaken in order to discover whether after the passage of an electric current through a piece of selenium any distinct evidence of polarization could be detected. It was then found that, after passing the current from a voltaic battery for some time through the selenium, and after having disengaged the electrodes from the battery and connected them with a galvanometer, a current, in some cases of considerable intensity, in the opposite direction to that of the original battery-current, passed through the galvanometer. This proved that the passage of the battery-current sets up polarization in the selenium.

All the results hitherto described were obtained with the selenium kept in the dark.

We then tried to discover whether on exposing the selenium to light during the passage of the polarization-current any change in the intensity of that current would be produced: we found that in several cases there was a distinct change; in most instances the action of the light assisted the passage of the current; but in one case we found that the effect of light was not only to bring the deflection of the galvanometer-needle down to zero, but also to send it up considerably on the other side.

Here there seemed to be a case of light actually producing an electromotive force within the selenium, which in this case was opposed to and could overbalance the electromotive force due to polarization.

The question at once presented itself as to whether it would be possible to *start a current in the selenium merely by the action of light.* Accordingly the same piece of selenium was connected directly with the galvanometer. While unexposed there was no action whatever. On exposing the tube to the light of a candle, there was at once a strong deflection of the galvanometer-needle. On screening off the light the deflection came back at once to zero.

This experiment was repeated in various ways and with light from different sources, the results clearly proving that by the action of light alone we could start and maintain an electrical current in the selenium.

All the pieces of selenium hitherto used had repeatedly had electrical currents passing through them, and it therefore seemed desirable to examine the effect of exposure to light on pieces of selenium which had never before had an electrical current sent through them.

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Accordingly three pieces were prepared, as nearly alike as possible, and were annealed. Two of them were found on trial to be sensitive to light—that is to say, light impinging on them produced an electrical current. The third piece, however, showed no signs of sensitiveness. Hence it appears that three pieces which were made up from the same stick, which are of the same length and were annealed at the same time, may, owing to some slight difference in their molecular condition, be very different as to their relative sensitiveness to the action of light.

In the experiments by which the above results were obtained, the piece of selenium under examination had always been exposed as a whole to the influence of the light, so that it was not possible to tell whether any one part of a piece was more sensitive than any other.

In order to examine into this point more fully, we used the lime-light, and then by means of a lens the light was brought to a focus on the particular portion of the selenium plate which was to be tested. A glass cell containing water, and having parallel sides, was interposed in the path of the beam, so as to assist in absorbing any obscure heat-rays.

The results of these experiments proved conclusively the following points:—

(1) That pieces of annealed selenium are in general sensitive to light, *i.e.* that under the action of light a difference of potential is developed between the molecules which under certain conditions can produce an electric current through the substance.

(2) That the sensitiveness is different at different parts of the same piece.

(3) That in general the direction of the current is from the less towards the more illuminated portion of the selenium, but that owing to accidental differences in molecular arrangement this direction is sometimes reversed.

The currents produced in the selenium by the action of light do not resemble the thermoelectric currents due to heating of the junctions between the platinum electrode and the selenium; for in many cases the current produced was most intense when the light was focused on points of the selenium not coinciding with the junctions; also the current was produced suddenly on exposure; and on shutting off the light the needle *at once* fell to zero: the gradual action due to gradual cooling was entirely wanting.

When the light fell upon a junction, the current passed from the selenium to the platinum through the junction, which is not in accordance with the place assigned to selenium in the thermoelectric series of metals.

Experiments were next undertaken in order to examine what effect would be produced on the strength of a current which was passing

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through a piece of selenium in the dark when a beam of light was allowed to fall upon it.

The results obtained from these experiments were as follows :—

With pieces of selenium of low resistance and with a weak current passing through them—

(1) When light falls on the end of the selenium at which the current from the positive pole of the battery is entering the metal it *opposes* the passage of the current.

(2) When light falls on the end of the selenium at which the current is leaving the metal it *assists* the passage of the current.

With pieces of selenium of a high resistance we found that in all cases the action of light tended to facilitate the passage of the battery-current, whichever was its direction.

We also found that in those pieces which appeared so little sensitive to light that no independent current was developed in them by exposure, yet when a current due to an external electromotive force was passing through them, the exposure to light facilitated the passage of the current.

The results of the experiments described in this paper furnish a possibie explanation of the character of the action which takes place when light falls upon a piece of selenium which is in a more or less perfect crystalline condition.

When a stick of vitreous selenium has been heated to its point of softening, if it were possible to cool the whole equally and very slowly, then the whole of the molecules throughout its mass would be able to take up their natural crystalline positions, and the whole would then be in a perfectly crystalline state, and would conduct electricity and heat equally well throughout its mass. But from the nature of the process it is evident that the outer layers will cool the most rapidly, and we shall have, in passing from the outside to the centre, a series of strata in a more and more perfect crystalline condition.

Light, as we know in the case of some bodies, tends to promote crystallization, and, when it falls on the surface of such a stick of selenium, probably tends to promote crystallization in the exterior layers, and therefore to produce a flow of energy from within outwards, which under certain circumstances appears, in the case of selenium, to produce an electric current.

The crystallization produced in selenium by light may also account for the diminution in the resistance of the selenium when a current from a battery is passing through it, for in changing to the crystalline state selenium becomes a better conductor of electricity.