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of the ebonite prism traversed by the intermittent beam must have been about one fourth of an inch. We are afraid that that figure is liable to give this misconception; in drawing it we were merely paying attention to the directions of the incident and refracted beam, and not to the actual thickness of the ebonite, which was in fact very small indeed where the intermittent beam passed through it.

XXXVI. *The Microphonic Action of Selenium Cells.*

By Dr. JAMES MOSER*.

WHEN I began these researches on the Transformation of the Energy of Light into that of Sound by the Photophone, I held the opinion which is still common, that there are two kinds of photophones and three forms of light-rays. My experiments led me to the conclusion that there is only one way in which light acts photophonically. The effect of radiation on selenium cells is, in fact, the same as that exerted on the majority of solid, liquid, and gaseous bodies used as non-electric photophonic receivers. Though rays may have different wave-lengths, all rays are the same in kind. There are not three kinds—heating, luminous, and chemical, but one and the same ray may have heating, chemical, and luminous effects.

In February last, when I began these experiments, I believed that the photophone could inform us as to the direct correlation between light and electricity. A current circulating around a beam of polarized light changes the plane of its vibration. Hence we are led to conjecture that there may exist further relations between light and electricity, and that, as the electric current or lines of magnetic force affect the beam, so, inversely, the beam may influence the electric current or the magnetic lines of force; and we may conjecture that such influence may manifest itself in the photophone.

I therefore tried to change the magnetic condition of an iron plate by light. I hoped, for instance, to get an electric current in the coil of the telephone at the moment when

* Read June 25, 1881.

its iron plate is exposed to radiation. I did not succeed in observing such a current.

Prof. W. G. Adams was the first to show that selenium on illumination develops an electromotive force. Still supposing that in the photophone a direct correlation between the energy of light and that of the electric current might reveal itself, I endeavoured to observe and to measure the electromotive force developed in selenium cells on their exposure to light.

I made selenium cells according to the method of Bell and Tainter as modified by Bidwell. Two thin copper wires were wrapped parallel side by side several times round a strip of mica. Selenium was then melted, and crystallized between them. In this way I obtained cells which were very sensitive and yielded, when connected with the battery, a clear sound in the telephone. According to my last measurement, the resistance of one of those cells in the dark is 3000 ohms, diffuse daylight reducing it to 2700. The measurements were made with an astatic-mirror galvanometer, the resistance of the coils of which was 6860 ohms. The scale was about one metre distant from the mirror, each division one fortieth of an inch. There were other galvanometers at my disposal, and a battery of twenty Leclanché cells. The galvanometer proved itself more sensitive than the telephone.

The above-mentioned selenium cell yielded by intermittent radiation of lime- or electric light clear and distinct sounds ; illumination by the same sources of light deflected the image of the slit strongly.

But the same light which, when a current of an external battery flows through the cell, makes the telephone to sound or the spot of light to slide along the whole scale, is not able to produce an observable electromotive force in the selenium cell. This non-appearance of a current (the circuit being formed only of selenium cell and galvanometer, or of selenium cell and telephone) is, in my opinion, very noteworthy ; for the problem which I wish here to solve is not to make photophones without batteries, but to explain the efficiency of the selenium cells by the qualities they actually possess.

It is possible to prepare pieces of selenium which show an electromotive force on being illuminated. I shall return to

this point further on. But cells and pieces of selenium *not* possessing this property nevertheless show photophonic action. Therefore the photophonic action cannot be explained by this property, which is, or at least may be, wanting in the selenium cells.

I proceeded further, always endeavouring to find a correlation of the energies. The current flowing through a selenium cell experiences a counter force—a polarization. I tried to observe, and, as far as possible, to measure it. This polarization is shown by *all* my cells and preparations of selenium. I found it, however, when measured by the compensation method, to be only about the thousandth of a volt. In order to observe the polarization as near as possible to its maximum, I employed a rotating switch, which I constructed by means of two alternating tooth-wheels, and which changed the current eighty times per second.

I next endeavoured to increase the electromotive forces originating in the selenium cell, as well as those produced eventually by light. I tried to attain this by taking the two wires of different material; then I prepared selenium pieces where selenium was simply between two straight parallel wires. At first I made a selenium cell, just like the one described above, replacing, however, the one copper wire by one of platinum, so that the selenium was between copper and platinum. But the polarization, which again could be easily observed, was here also very small. On measuring, it was found again about one thousandth of a volt. Also this cell did not produce, either in the dark or on illumination, any current which could be observed by the galvanometer.

In order to increase the polarization, I gave the polarized selenium cell greater capacity. I took, instead of the wires, two larger plates, each 6 centim. long, 3 centim. wide, and about 1 millim. thick. My intention was to begin the experiments with three of such pairs, with

copper, selenium, copper;
zinc, selenium, zinc;
zinc, selenium, copper.

With the latter of these cells I succeeded (after having sent through it the current of a strong battery) in observing

a polarization of about 0·4 volt. The cell had now become a polarization battery, giving rise to a current long after it was separated from the primary battery.

In all these experiments, and especially in the last, a superposition of polarizations could be distinctly observed ; so that here we have to deal, not simply with thermo-electric currents, but with electro-chemical decomposition.

An observation, however, which I now made gave a different direction to these researches. But their aim remained unchanged—namely, to explain the efficiency of the selenium cells, to understand the transformation of energy of light into that of sound in the selenium cell, regarding it from a more general point of view and not merely as an isolated phenomenon in selenium, but, by finding the general law, to remove selenium from its isolated position. This, however, may be done either by comparing other bodies with it (which is the method of previous investigations on the subject, and was my own also till now), or this may be effected by inserting selenium in the series of other bodies. The latter method I shall now describe.

I intended to make such cells of copper, selenium, copper, or of zinc, selenium, copper plates, in the same way as the above-described photophonic cells. On a copper plate I melted amorphous selenium, and put on it the second metal plate of zinc or copper. Then I heated gradually, so that the selenium became crystalline; and I then annealed it. Whilst the amorphous selenium adheres very well to the metal plates, these cells proved very brittle when the selenium was crystalline ; the selenium always split off from the copper plate. In order to find how to avoid this splitting-off, I examined the matter more closely; thus, I left out the second metal plate, and experimented with copper and selenium only.

The preparation was, in accordance with that of the photophonic cells, the following:—One of the copper plates to be used for the cells was heated on a large brass plate of about 3 millim. thickness ; this was covered by a thin sheet of mica, on which the selenium which eventually flowed off was collected. The copper plate having reached the melting-point of amorphous selenium, was covered with this substance and thereupon removed from the brass plate. On being re-

moved it cooled quickly; and on it now a black brilliant layer of amorphous selenium remained. The larger brass plate having also cooled, the copper plate covered with selenium was again laid on it and again slowly warmed, so that the selenium crystallized. The temperature was still further raised, near to the point at which the crystalline selenium begins to melt. The selenium was then annealed.

But, notwithstanding this caution, it was not possible to fix the selenium on the copper plate. It exfoliated and split off. Every lamina which exfoliated was on the upper side light grey, and on the lower side blue-black, not brilliant but dull. In the same way the copper plate had now a similar dull blue-black covering. This blue-black body is cuprous selenide, Cu_2Se . There were thus three layers—copper, cuprous selenide, and selenium; and in the copper-selenium-zinc cell two other layers—selenide of zinc and zinc; so that all together there were five layers.

I took thinner copper plates; but the splitting-off still occurred.

This experiment shows that between the copper and the selenium, or rather the cuprous selenide, there is only a slight and imperfect contact.

But the same is the case in the photophonic cell. In this also the three layers—copper, cuprous selenide, selenium—follow one after the other. The plates give only an enlarged view of what is to be observed in the photophonic cell on a smaller scale, and with more difficulty, by the eye. Thus we see that in the photophonic selenium cell also we have only a similar slight and imperfect contact, which is to be influenced by radiation. It was first by this experiment that it became obvious to me that a microphonic effect is the essential part of the action of the selenium cells.

I was confirmed in this conclusion, that *the selenium photophone is a microphone*, when I learned that Mr. Sumner Tainter had constructed a photophone in which selenium was replaced by carbon. Indeed his apparatus, the zigzag line filled with carbon on the silver-coated glass plate, is nothing else than a microphone. If we remember the apparatus described by Mr. Hughes as a thermoscope, we understand that the selenium photophone of Messrs. Graham Bell and Sumner Tainter

agrees in its principle with the carbon photophone of the latter; and, again, this is in its main features the same as the thermoscope.

Thus my attention became now more directed to those passages in the literature where the degree of the resistance at the surfaces of contact between the selenium and the metal, in comparison with the total resistance, is discussed.

In 1875, before the invention of the microphone, Dr. Werner Siemens observed a high resistance at the surfaces of contact. He arrived at the conclusion "that an essential part of the resistance of the selenium is in its limiting layers at the surfaces of contact"*.

Mr. Sabine is of the same view. Finding, *e. g.*, in one piece of selenium with several transversal platinum wires the resistances of the junctions to be 429, 479, 498, and 428 megohms, the resistance of the selenium itself between the wires, however, much smaller (22, 13, and 0 megohms), he remarks:—"It is clear from these measurements that a large portion of the observed resistance of a so-called selenium resistance may, and frequently does, reside in the junctions, and not in the selenium. Therefore the larger we make the surface of contact between the platinum and the selenium, the less likely are we to find an otherwise sensitive piece of selenium rendered comparatively insensitive by the introduction of high junction resistance. In this respect the form of selenium plate designed by Dr. Werner Siemens, in which the platinum wires form gratings or interlying spirals, is unquestionably the best form to employ when the object in view is to obtain a high sensitiveness to light"†.

Both authors assume the selenium to possess a special sensitiveness, and this quality to be damaged by the high resistance of the junctions. Therefore they aim at annihilating this resistance at the surfaces of contact. Aiming at this annihilation, they enlarge the surfaces of contact and thus diminish the resistance.

The surfaces of contact should indeed be enlarged. The reasons, however, for which this must be done are, in my opinion, just the opposite to those influencing these two

* Pogg. *Ann.* clix. p. 140.

† 1878, *Phil. Mag.* (5) v. p. 404.

observers. It is the high resistance at the junctions which is the variable, and which is necessary for the microphonic action. The case of this resistance alone being the variable I shall discuss immediately. That the resistance at the junctions is high is a necessary consequence of the imperfect and variable contact. To annihilate it is to render the telephone insensitive. And, *vice versâ*, the more extensive the surfaces of contact are, the more sensitive is the selenium cell.

A further strong support, amongst others, is given to this theory by the observation of Mr. Bidwell*, who has made very numerous experiments with selenium cells. "He got the best speech from cells of high total resistance . . . The selenium should, however, have a low specific resistance."

These observations are easily understood by the microphonic action of the cells; for, that the total resistance is to be great and yet the specific resistance of the selenium is to be small, has no other meaning than that there must be a bad contact between good conductors.

The next question is, if this microphonic action is confined only to the surfaces of contact. I must here recall that Messrs. Draper and Moss†, distinguishing three crystalline modifications of selenium, observe as to their conductivity, "Between these two forms of granular selenium—the apparently nonconducting and the comparatively highly conducting—there is another, of intermediate resistance. This modification is highly sensitive to light."

Just so, according to Rammelsberg‡, selenium exists in four allotropic modifications, three of which are crystalline.

For evidence of the microphonic action I was at first contented to observe that selenium in this crystalline state, in which it is most brittle and the most powdery, is also most sensitive to light. Afterwards I succeeded in obtaining a piece which shows this very clearly. Between two platinum wires of 3 centim. length was a selenium plate 8 millim. in width and hardly 1 millim. in thickness. Heated in air and annealed, the whole surface had taken the light grey colour of a crystalline state; half the upper surface, on

* London Phys. Soc. Jan. 22, 1881; Tel. Journ. ix. p. 52.

† 1873, Proc. Irish Ac. (2) i. p. 533, Nov. 10.

‡ 1874, Pogg. Ann. clii. p. 151.

the side of the one platinum wire, was smooth and continuous; the other half, near the other platinum wire, was powdery and granular. Alternately one of the two halves was kept constantly dark, and the other half at the same time intermittently illuminated. Thus I could observe that almost the total sensitiveness of the whole plate resided in the granular coarse half of the surface. This shows that microphonic effects occur also in the selenium itself. But even if the selenium were perfectly homogeneous, and remained so during the illumination, the rays would produce heat and change of volume, which would have a microphonic influence on the contact.

By such microphonic changes the efficiency of the selenium cell would be explained, and thereby the selenium would be removed from its isolated position and coordinated with all the other bodies in which change of volume and of form under the influence of radiation have been observed.

I, however, do not deny that light may have other effects on the selenium. That such is the case is indeed one of the causes which have hitherto masked the microphonic action of the cells. That my present view of the simple action of the selenium did not present itself at once is owing to two causes.

In the first place, there is the fact that the microphonic variations or changes in volume and in form, attributed commonly to the so-called heat-rays, are produced in the selenium by the illuminating rays.

In the second place, complication is introduced by the fact that selenium exists in four allotropic modifications, and that light is able to exert on these divers influences. Though these are not essential to the action of the photophone, it has nevertheless been assumed by others, and at first by myself, that such changes might be the key for the explanation of the selenium photophone.

Of these two impediments which stood in the way of the perception of the microphonic action of the cells, I intend to speak more in detail. And first a few words on what, for the sake of brevity, may be called the heating effect of the light-rays.

In the beginning of April* I repeated the experiment of Mr. Graham Bell, and allowed light to pass through ebonite.

* Lond. Phys. Soc. April 9, 1881; 'Nature,' xxiii. p. 595.

In order to be able to make a quantitative observation I connected the selenium cell, on which the light was to fall, not only with the telephone, but also with a galvanometer. While, however, it appeared that a photophonic effect took place through the ebonite, it was shown that this effect was only a small part of the direct effect when the ebonite diaphragm was away. Now, as ebonite allows passage only to red and ultra-red rays, we learn from this experiment two things:—

(1) That the illuminating rays are those which are especially absorbed by selenium, and that these produce the greater part of the photophonic action.

(2) That it is even possible to make a *selenium photophone without light*—that is, with exclusion of illuminating rays and by the influence of heat-rays only.

That there is simply a heating effect of the illuminating rays in the selenium photophone has perhaps not yet been sufficiently insisted on, because the most modern researches on light-rays are not yet assimilated to the general view of physics. We find still the conception of three different kinds of rays—heating, illuminating, and actinic; whilst it has long been demonstrated that there is only one form of rays, differing from one another, however, in wave-length and intensity. On the body on which the ray falls depends whether its energy is perceived as heat, or light, or chemical effect. In order to be effective a ray must be absorbed. The bodies, however, on which the rays fall select the rays they absorb in the most various manner, which we recognize by the endless varieties of absorption-spectra. The absorbed rays alone are able to exert an effect; they only can warm the body. And heating occurs not only by red and ultra-red rays, but by the rays which are absorbed. Only the absorbed rays can produce (and that is the point in question here) changes of volume and of shape, and in this way influence the contact of current-conducting parts.

As the last-mentioned experiment demonstrates, selenium absorbs principally the illuminating rays. When, therefore, selenium is exposed to radiation, the change of volume and of shape is produced chiefly by the illuminating rays; *selenium is heated by light*. It must be the illuminating rays which make the selenium cell act microphonically.

That light, however, may produce in selenium other changes than heat and deformation, which are essential to the efficiency of the selenium cell, has been the second cause which masked the microphonic action of the cell. These are changes in the material; they concern rather the chemistry of selenium. They are indeed purely chemical if we view the existence of selenium in four allotropic modifications as a chemical quality. Into these chemical changes I shall enter here only so far as it is necessary for the proof that they are not essential to the microphonic action of the selenium cells, since my aim now is the physical one of correlating two forces.

When, now, we no longer consider the selenium cells especially, but selenium in general, we find that light can produce in it, if the selenium is an element and pure*, no other chemical changes than those which induce the transformation of one of the allotropic modifications into another one. But such a transformation is connected with development of energy; for in 1851 M. Hittorf† observed a rise of temperature of 90 degrees when the vitreous modification changed into the crystalline; and Regnault‡ (1856) in a similar case, observed an elevation of temperature of 130 degrees. With a proper arrangement (that is, in a closed circuit) we shall get, instead of the development of heat, an electric current—just as, for instance, two solutions of the same salt, but of different concentration, on being mixed together, give a development of heat, but, when brought into a circuit in a proper manner, produce electricity equivalent to this heat.

I have already mentioned above that Prof. W. G. Adams thus observed electromotive forces on illuminating selenium connected only with a galvanometer, but that generally the photophonic cells do not give such a development of electricity, and that therefore this property of selenium cannot be used

* On melting selenium, a grey film was formed on the surface. This being removed by a platinum spatula, the amorphous selenium showed a brilliant surface; and only such selenium was employed, in order to get congruent results.

Selenium crystals of 3 millim. length were obtained by sublimation on the cover of the crucible. At first amorphous selenium condensed; afterwards these sublimated crystals, which were insoluble in water, were formed.

† Pogg. *Ann.* lxxxiv. p. 216.

‡ *Ann. Chim. et Phys.* (3) xlv. p. 284.

for the explanation of the efficiency of the photophonic cells. (Here I will add that of course thermoelectric currents can be produced by differential heating of the two junctions. In order to get such a great difference of heating, the cell must be exposed to greater heat. Thus I brought near the focus of the sun's rays only one small part of the cell, and found a small deflection of 10 divisions, or about half a centimetre.)

That by radiation the allotropic modification of selenium may be changed, but that such changes do not occur in the selenium cells, was proved most conclusively by one piece of selenium, which had the anomalous property of showing increased resistance on being illuminated.

Till now I had prepared all selenium cells and all pieces of selenium as I have described above, in the open air or in an air-bath. I never succeeded in obtaining selenium pieces of such low resistance as Messrs. Adams and Day got in three of their pieces, the resistances of which were 55, 58, 68 ohms. These three pieces differ, it is true, strongly from most of the other pieces in their resistances, which were as high as 7,600,000 ohms. I therefore followed their method almost literally. I laid several pieces of amorphous selenium, furnished with platinum electrodes and wrapped in paper, for twenty-four hours in sand which had been warmed before by a red-hot iron ball,—a process in which the influence of the aqueous vapour evolved from the paper is not excluded. In this way I got, indeed, pieces of the comparatively low resistance of 700 and 2000 ohms; whilst that of the other pieces prepared at the same time amounted still to 350,000 ohms.

The selenium piece of lowest resistance (700 ohms) showed at first so variable a resistance, that this could scarcely be measured. Then, when it became more constant, a determination of 700 ohms was possible. But on exposure to light, the resistance *increased*. This behaviour is just the opposite of what all my other cells or pieces of selenium show. And it is equally in contradiction to the diminishing of resistance found in all other cases by all other observers; only Messrs. Adams and Day mention at the end of their numerous observations, that one single piece out of the great series behaved like this of mine, increasing its resistance on being illuminated. This piece of mine in which I observed this anomalous quality, exhibited in general the tendency to rise

steadily in resistance; so that there occurred, on illuminating it, a continuous increase of resistance, and, on darkening, a feeble but never a complete return to the original value. Every exposure to light again renewed this increase; and even a slight shaking of the table changed the resistance. This tendency to increase the resistance was manifested so strongly, that on the following day I found the resistance had risen from 700 to 5600 ohms.

But this piece of selenium showed still another anomaly, contributing, however, to the explanation of the first. I intended to examine the polarization produced in the selenium by the primary battery-current when separated from the battery and connected with the galvanometer by means of a switch. And now I found a secondary current which went through the galvanometer always in the same direction, quite independent of the direction of the primary battery-current. Even when the primary current was produced by a single Leclanché cell only, the deflection by the secondary current was 80 divisions, or about 5 centim. This secondary current is therefore no polarization-current; for in that case its direction would be always opposite to the primary. But here a change of direction did not occur, the secondary current always flowing from the platinum electrode A to the platinum electrode B, and never in the opposite direction.

The passage of a current also, like illumination or concussion, occasioned a quicker increase of resistance.

All these qualities, however, are very easily understood; and the very appearance of the piece suggests the explanation. There are in it several modifications of the selenium side by side. At the transformation of the one modification into another, as I have pointed out above, heat or electric effect must take place. A state of equilibrium is not reached before that modification has been formed the formation of which is attended by the maximum development of energy—thermal or electric. Such modification again, as also mentioned above, has a different resistance from the one from which it originated; and therefore the variation of resistance is a necessary consequence of the change of modification. While the transformation goes on, we observe the electric current; after the transformation is complete we observe the change of resistance.

Such changes in the modification can be also occasioned by light: a pencil of amorphous selenium assumes, when exposed to the daylight, a grey crystalline surface.

Two conditions distinguish these changes from the photophonic ones, and prove that, as a rule, they do not occur in the photophonic cells.

On darkening the cell in which only a microphonic action took action, the original state was reached again which it had before being illuminated; in the piece of selenium wherein a change of modification occurred, this was not the case. This is the reason why the light-spot returns to its original position on the galvanometer-scale in the case of the selenium cell, but does not in the case of the selenium piece. And, secondly, by such changes of modification a phenomenon is produced which has been called "fatigue." Such fatigue (that is, an insensitiveness) must take place as soon as the store of the one modification which is transforming itself into the other is exhausted. But it cannot take place if we have to deal with a microphonic action alone. And, indeed, in the selenium cells I never could observe this fatigue. The sensitiveness of the last-described piece is now extremely lowered.

And thus we see that there are two different effects which light may have on selenium and on selenium cells. The one is more of a chemical, the other more of a physical character. The one is a changing of modification, and is not essential to the efficiency of the selenium photophone. In this latter we have to deal essentially with a heating effect, changing volume and contact—in brief, with a microphonic action.

Therefore, as to the photophonic efficiency of selenium, I see no reason to separate it from all other bodies; and I no longer believe that there is any prospect of finding an unknown power or a new relation of forces in this substance.

The above experiments were performed in Prof. Guthrie's Physical Laboratory at the Science Schools, South Kensington. The permission granted me, at his request, by the Department of Science and Art to carry out my ideas experimentally is only one of the many acts of kindness and courtesy which I have received from scientific men and Societies during my sojourn in England.

Physical Laboratory, South Kensington,
June 1881.