



## XXII. On the sensitiveness of selenium to light, and the development of a similar property in sulphur

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To cite this article: Shelford Bidwell M.A. LL.B. (1885) XXII. On the sensitiveness of selenium to light, and the development of a similar property in sulphur , Philosophical Magazine Series 5, 20:123, 178-191, DOI: [10.1080/14786448508627741](https://doi.org/10.1080/14786448508627741)

To link to this article: <http://dx.doi.org/10.1080/14786448508627741>



Published online: 29 Apr 2009.



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resolves itself into the plotting of the two curves  $r = \phi(\theta)$ ,  $r = \psi(\theta)$ , between the limits  $\theta = \alpha_1$ ,  $\theta = \alpha_2$ , the fixing of the instrument so that its axis passes through O, the pole chosen in plotting the curves, the driving of the two pointers  $S_1$  and  $S_2$  along the two curves (which is easily done by one person) causing  $S_3$  to trace a third curve between the same limits; then the clamping down of  $S_1$ , the forcing of  $S_3$  to follow back its former track, and the reading of the revolutions of the wheel attached at  $S_2$  during this last part of the performance. This reading gives the required value of the integral when the scales on which the two curves were drawn are taken into account. These scales must be chosen so that the maximum difference between  $OS_1$  and  $OS_2$  shall at least not be greater than the diameter of the circle whose radius is  $OS_1$ . In the above description, the word collar is used to mean any form of connection that allows with as little friction as possible one degree of relative freedom.

Melbourne, June 1, 1885.

XXII. *On the Sensitiveness of Selenium to Light, and the Development of a similar Property in Sulphur.* By SHELFORD BIDWELL, M.A., LL.B.\*

THE remarkable property apparently possessed by crystalline selenium of having its electrical resistance varied by the action of light, a property which was first announced by Mr. Willoughby Smith in 1873, has been the subject of many investigations†. Of these the best known, and by far the most exhaustive, are the researches of Prof. W. G. Adams and Mr. R. E. Day, an account of which is published in the Phil. Trans. of 1877. As the result of numerous experiments, these gentlemen were led to form the opinion, that "the electrical conductivity of selenium is electrolytic"‡. The principal reasons given for this conclusion are:—(1) that the resistance of the selenium-bars used appeared to depend upon

\* Communicated by the Physical Society; having been read at the Meetings on May 23 and June 13.

† Willoughby Smith, Journ. Soc. Tel. Eng. ii. p. 31; Earl of Rosse, Phil. Mag. March 1874, p. 161; Sale, Proc. Roy. Soc. 1873, p. 283; Phil. Mag. March 1874; Werner Siemens, Phil. Mag. November 1875, p. 416; Draper and Moss, 'Chemical News,' xxxiii. p. 1; Adams and Day, Proc. Roy. Soc. 1876, p. 113; Phil. Trans. 1877, p. 313; C. W. Siemens, Proc. Roy. Inst. 1876, p. 68; Sabine, Phil. Mag. June 1878, p. 401; Graham Bell, 'Nature,' xxii. p. 500; Shelford Bidwell, Phil. Mag. April 1881, and January 1883; Fritts, 'Electrical Review,' March 7, 1885, p. 203.

‡ Phil. Trans. vol. 167, p. 328; Proc. Roy. Soc. 1876, p. 115.

the electromotive force of the battery employed, being generally diminished as the battery-power was increased; (2) that the resistance of a bar AB was generally not the same for current in the direction AB as for a current in the direction BA; (3) that the passage of a battery-current was always followed, when the battery had been disconnected, by a secondary or polarization-current in the opposite direction, it being clearly proved that this secondary current was not due to any thermoelectric action, either in the selenium itself or in any other part of the circuit.

The authors do not, however, appear to have considered that the observed behaviour of selenium was to be explained by actual electrolysis, but rather that the molecular structure or crystalline condition of the substance was altered or modified by the action of a current of electricity in such a manner as to produce effects analogous to those which would have occurred if the selenium were an electrolyte and actually decomposed by the current. As to the possible influence of light, the following are their words\*:—"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, 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."

Attention has lately been again directed to the subject of selenium, and its behaviour under the influence of light, by the publication, by Mr. C. E. Fritts of New York, of a new and extremely ingenious method of constructing selenium cells†. He melts a thin film of selenium upon "a plate of metal with which it will form a sort of chemical combination. . . . . During the process of melting and crystallizing, the selenium is compressed between the metal plate upon which it is melted and another plate of steel or other substance with which it will not combine. . . . The non-adherent plate being removed after the cell has become cool, [he] then covers that surface with a transparent conductor of electricity, which may be a thin film of gold-leaf. . . . The whole surface of

\* Proc. Roy. Soc. 1876, p. 117.

† Proc. American Assoc. 1884. Reproduced in the 'Electrical Review,' March 7, 1885, p. 208.

the selenium is therefore covered with a good electrical conductor, yet is practically bare to the light, which passes through the conductor to the selenium underneath." The sensitiveness to light of cells constructed in this manner seems to be far in excess of anything that has been previously obtained; and the "photoelectric" currents which (like the selenium bars of Messrs. Adams and Day) they are capable of originating, are said to be strong enough to be actually useful in practical work.

It is impossible to read Mr. Fritts's paper without being impressed by the resemblance of some of the phenomena which he describes to those of electrolysis. The mere arrangement of the apparatus—two metallic plates with a third substance between them—is in itself strongly suggestive; while the unequal resistance offered by the two surfaces, and the generation of an independent electromotive force, in conjunction with the polarization-effects above referred to\*, make it hard to believe that the conduction of selenium (in the form used in experiments) is not truly and literally electrolytic.

The only considerable difficulty in the way of this hypothesis arises from the fact that selenium is not an electrolyte. Ever since its discovery in 1817, selenium has been regarded as an element, and very strong evidence indeed would be necessary to deprive it of its elementary character; this is perhaps the reason why the electrolytic theory has not previously been proposed. But there is a possible way out of the difficulty, which was suggested to me by the first words in the above quotation from Mr. Fritts's paper. He spreads the selenium upon a plate of metal *with which it will form a chemical combination*. Now selenium will, I believe, combine more or less easily with all metals, forming selenides; and in experiments upon the conductivity of selenium, it has been usual to submit the substance to prolonged heating in contact with metallic electrodes. This prolonged heating (generally followed by slow cooling) has hitherto been called "annealing;" and the undoubted fact that it diminishes the specific resistance of the selenium and increases its sensitiveness to light, has been explained by supposing that the process is favourable to perfect crystallization.

I venture to suggest, as the true explanation of the effect, that heating is favourable to a chemical combination between the selenium and the metal forming the electrodes, that a selenide is thus formed which completely surrounds the elec-

\* "The existence of polarization," says Clerk Maxwell, "may be regarded as conclusive evidence of electrolysis." 'Electricity,' vol. i. p. 363.

trodes, and is perhaps diffused to some extent throughout the mass of the selenium\*; and that the apparently improved conductivity of the selenium, together with the electrolytic phenomena which it exhibits, are to be accounted for by the existence of this selenide.

I have sometimes been tempted to think it possible that the apparent conductivity of selenium may in fact be *entirely* due to the impurities which it contains, and that perfectly pure selenium would be as good an insulator when in the crystalline form as it is in the vitreous condition. Vitreous selenium might contain a large percentage of conducting particles without sensible increase of its conductivity, but that this would not be the case with crystalline selenium, is rendered more than probable by the results of some experiments which I have described in a former communication†. If a conducting powder, such as graphite, is mixed with melted sulphur, even in small proportions, the mixture when cold is found to conduct electricity; while if a very large proportion of the same powder is incorporated with melted shellac, the shellac when cold remains sensibly as perfect a nonconductor as if it were pure. The explanation which I have given of these facts, and in support of which a number of experiments are quoted, is as follows:—The first mixture does not consist of a uniform structureless mass of sulphur, having particles of carbon imbedded in and completely surrounded by it: it is in fact an aggregation of little crystals of sulphur with carbon packed between them like mortar between bricks. The conduction thus takes place entirely through the carbon particles, which may be considered as extending in a series of chains from end to end of the mass. In the case of the shellac mixture, though the proportion of carbon may be larger than in the sulphur experiments, the resistance is still sensibly infinite, because the structureless shellac penetrates between and completely surrounds the carbon particles. Just in the same manner, selenium, when in the vitreous condition, would completely surround any particles of conducting selenides which it might contain; while, when the selenium was crystallized, the conducting particles would arrange themselves in the form of a network, capable of conveying a current of electricity.

Selenium which is free from impurities appears not to be an article of commerce. An analysis of samples collected by Professor Graham Bell from different parts of the world

\* The selenium is necessarily for some time in a liquid state.

† Phil. Mag. May 1882, p. 347.

disclosed the presence of the metals iron, lead, and arsenic\*, all of which would form conducting selenides. Nevertheless I thought it would be worth while to ascertain roughly the specific resistance of a piece of selenium which, since it has come into my possession, has never been in contact with metal. The selenium (which was supplied by Messrs. Hopkin and Williams) was melted in a mould built up of slips of glass, crystallized and "annealed" in the usual way; but, contrary to the general practice, it was *not* fitted with metallic electrodes before annealing. A plate of crystalline selenium was thus formed, having a thickness of about 2 millim. and a superficial area of 1 square centim. The two opposite surfaces were rendered smooth and clean by rubbing them upon a flat board covered with fine glass-paper, and the plate was placed between two layers of thick tinfoil which were pressed into good contact with it by a weight of 500 grammes. When this arrangement was connected in circuit with 6 Leclanché cells and a reflecting galvanometer, a deflection was produced indicating a current of about  $\frac{1}{5}$  micro-ampere. Assuming the electromotive force of the battery to have been 10 volts, the resistance of the plate would be 500 megohms; and therefore the resistance of a cubic centimetre of the selenium between opposite faces (*i. e.* its specific resistance) would be 2500 megohms. From the dimensions and resistance of a good selenium cell with copper electrodes, which I have in my possession, I calculated that the specific resistance of the selenium contained in it was about .9 megohm. Thus, so far as the result of a single rough experiment can be trusted, it appears that the conductivity of selenium which has been annealed in contact with copper is nearly 3000 times greater than that of selenium which has undergone similar treatment without the presence of a metal. Whether selenium, when perfectly pure, is altogether a non-conductor, would be an interesting question for an expert chemist to determine†. It is sufficient for the theory which I am at present advocating that its specific resistance should be very high.

By assuming the admixture with the selenium of metallic selenides, an explanation is afforded of the following facts:—

- (1) The diminished resistance produced by annealing.
- (2) The fact, first pointed out by Graham Bell, that the resistance of selenium appears to depend greatly upon the nature of the metals of which the electrodes are formed. For obtaining low resistance he recommends the use of brass in

\* Paper read before the National Academy of Sciences, April 21, 1881.

† On more mature consideration I am inclined to think that it is *not*.

preference to platinum, and expresses his belief that the chemical action between the brass and selenium contributes to the low resistance of his cells, "by forming an intimate bond of union between the selenium and brass."\*

(3) The fact observed by Adams and Day that there is generally a "diminution of resistance in the selenium as the battery-power is increased." The same phenomenon occurs in the mixtures of sulphur and carbon before referred to. It points to the existence of imperfect contact between conducting particles, the conduction partaking of the nature of disruptive discharge, and is consistent with the supposition that particles of conducting selenide are imbedded in the selenium †.

(4) The apparent production by a current through a piece of selenium of a "set of the molecules which facilitates the subsequent passage of a current in the opposite, but obstructs one in the same direction"‡. This would be accounted for by the electrolytic deposition of selenium (from the selenide) upon the anode.

(5) The polarization-effects, which would also proceed from electrolysis.

(6) "A slight increase of temperature of a piece of annealed selenium is accompanied by a large increase of electrical resistance"§. This also occurs in the mixture of sulphur and carbon, and is explained by supposing that the heat-expansion of the medium draws apart the conducting particles contained in it, causing them to have fewer points of contact with each other, and thus increasing the resistance of the whole ||. A more considerable rise of temperature so greatly diminishes the specific resistance of the selenide (and perhaps of the selenium) as to more than counterbalance this effect; and thus it happens (as I have shown in a former communication ¶) that selenium cells have a "temperature of maximum resistance," which is generally a few degrees above the average temperature of the air.

(7) The resistance of prepared selenium is generally greatly diminished by the action of time. Prof. Adams found that the average resistance of a number of pieces of selenium was

\* Lecture to American Assoc. 1880. Reprinted in 'Nature,' vol. xxii. p. 500.

† See "On the Electrical Resistance of Carbon-contacts," Proc. R. S. Feb. 1, 1883; and "On Microphonic Contacts," Journ. Soc. Tel. Eng. April 12, 1883.

‡ Adams and Day, Proc. R. S. 1876, p. 114.

§ Adams and Day, Phil. Trans. 1877, p. 342. See also Phil. Mag. Jan. 1883, p. 31.

|| Phil. Mag. May 1882, p. 351.

¶ Phil. Mag. April 1881.

reduced to less than one fortieth in the course of a year\*. During this period the selenium had been in contact with the metallic electrodes; and it seems possible that a larger quantity of selenide than was produced in the first instance by the process of annealing was slowly formed. This would especially occur at the "marked end," or anode, where there would naturally be a quantity of free selenium.

In the above argument it has been assumed that selenium will combine directly with any metal with which it is brought into contact, the combination being facilitated by the application of heat. In the case of such metals as copper, brass, and silver this is undoubtedly the fact. Indeed, an attempt to make a selenium cell with silver wires was attended with failure in consequence of the complete destruction of the metal after contact with the melted selenium for only two or three minutes. It is, however, questionable whether platinum (which was the metal used by Adams and Day) is, in any sensible degree, attacked by selenium either at the ordinary temperature or at that reached in the process of annealing. With sufficient heat the two substances will undoubtedly unite; and I have found that the surface of platinum-foil upon which melted selenium has been kept for an hour or two at a temperature probably of about  $250^{\circ}$  C. acquires a bluish-grey colour which may be due to selenide. But whether any appreciable quantity of selenide is formed in the ordinary preparation of crystalline selenium is a question only to be settled by the aid of refined chemical operations which I am incompetent to undertake, and in the meantime the suggested theory is left without direct confirmation.

But certain indirect evidence in support of my views has been forthcoming. Selenium is an element which, in its properties, closely resembles sulphur, and attempts have from time to time been made, hitherto without success, to develop in sulphur that peculiar sensitiveness to light which is such a remarkable characteristic of selenium. It occurred to me that if this property of selenium were really due to the accidental existence of metallic selenides, then the admixture with sulphur of metallic sulphides might be expected to lead to similar effects. It is not possible to "anneal" a stick of sulphur or a sulphur "cell" previously furnished with metallic electrodes, because sulphur does not, like selenium, solidify and crystallize at a higher temperature than that of its first melting-point. But if it is true that the virtue of annealing really lies in the fact that a chemical union of the two elements is promoted by the action of heat, it is clearly immaterial

\* Phil. Trans. *loc. cit.* p. 348.



whether the substances are heated together before or after the formation of the cell. Sulphur containing sufficient metallic sulphide to render it a conductor of electricity might be used in the construction of a cell which might be expected to be sensitive to light without any preliminary annealing. This turned out to be actually the case.

Silver was the metal chosen for the experiments on account of the facility with which it combines with sulphur.

*Cell No. 1.*—Five parts of sublimed sulphur and one part of precipitated silver were heated together in a porcelain crucible for about two hours. The mixture was from time to time stirred with a glass rod and was finally allowed to settle, so that the bulk of the sulphide and any free silver which might remain fell to the bottom of the crucible. When the temperature was slightly above the melting-point the liquid sulphur, which was perfectly mobile, though black with minute suspended particles of sulphide, was poured off for use. Two wires of fine silver\* were then coiled side by side around a strip of mica 50 millim. long and 27 millim. wide; the wires were about 1 millim. apart, and care was taken that they did not touch each other at any point. Some of the melted sulphur was spread evenly over one surface of the mica, the two wires being thus connected with each other through half their entire length by a thin layer of the prepared sulphur. When cold, this cell was connected in circuit with a battery and a galvanometer. It was found to conduct electricity, but its resistance was very high, being probably between 20 and 30 megohms. With the object of partially bridging over the intervals between the wires, the sulphur was melted by laying the cell upon a hot plate, and a piece of very thin silver-foil, measuring 25 millim. by 10 millim., was laid upon its surface: this was probably entirely converted into sulphide before the cell was again cold. The cell was now found by a bridge-measurement to have a resistance of 900,000 ohms†. Once more it was connected with a Leclanché cell and a suitably shunted galvanometer; the deflection was noted, and a piece of magnesium wire was burnt at a short distance from the sulphur. The deflection was immediately more than doubled; and when the magnesium was extinguished, the spot of light at once returned to very nearly its original position. The effect was almost as great when a glass trough containing a saturated solution of alum was interposed between the sulphur and the burning magnesium‡.

\* Supplied by Messrs. Johnson and Matthey.

† This resistance was afterwards found to be very variable, and it was never the same with a direct and a reverse current.

‡ This cell was exhibited in action at the Meeting of the Physical Society on May 23rd, and at the Soirée of the Royal Society on June 10.

Now it is well known that the resistance of sulphide of silver is greatly diminished by heat \*, and it was therefore important to ascertain whether the effect just described was due to light or to heat. To speak more accurately—Is it an effect of *radiation* or of *temperature*? Exposure to radiation, whether visible or invisible, is of course always accompanied by a certain rise of temperature, and confusion has sometimes arisen, especially in discussing the properties of selenium, from failure to distinguish between the direct effects of radiation, and the indirect effects which are primarily due merely to a rise of temperature†. In the photographic processes it is radiation *per se* that produces the observed results: in the best known processes, the effective rays happen to be those which correspond to the most-refrangible part of the visible spectrum together with the invisible rays beyond it. But by more recently discovered methods the “obscure heat-rays,” as they are sometimes called, have been made available for photographic purposes‡; and these do not act by virtue of any rise of temperature which they may cause, but exert direct chemical action upon the sensitized plate. Again, if a thermo-pile is exposed to radiation, an electromotive force is generated. Here, however, the effect of radiation is indirect; it acts only through the medium of the heat which it produces; and if an equal and similarly distributed amount of heat were communicated to the thermo-pile by any other means (as by conduction), exactly the same effect would follow. In an ordinary selenium cell radiation acts both directly and indirectly, tending to produce opposite effects. The direct effect of the radiation, whether it be visible or infra-red or ultra-violet, is a diminution of the resistance of the cell; at the same time the radiation slightly raises the temperature of the cell, and so indirectly tends to increase its resistance. If a selenium cell in circuit with a battery and a galvanometer is suddenly exposed, by withdrawing a screen, to the radiation of a black-hot poker, a momentary swing of the galvanometer-magnet will at first indicate a fall in the resistance; but this will be almost immediately followed by a rise which will increase up to a certain limit as the temperature of the cell becomes higher. The same kind of thing occurs when the cell is exposed to the infra-red or red portions of the spectrum; but in the latter case the temperature-effect merely diminishes, instead of overpowering, that directly due to radiation. If the bridge method is used for measuring

\* Faraday, Exp. Res. §§ 432-439.

† See Moser, Proc. Phys. Soc. 1881, p. 348.

‡ Captain Abney is said to have obtained a photograph of a kettle of boiling water by means of the invisible radiations which it emitted.

the resistance, it may easily happen that the effect of gradually rising temperature escapes notice, a balance not being obtained until the temperature has become constant; and thus, probably, is to be explained the fact that different observers have attributed the most powerful action upon selenium to different parts of the spectrum, ranging from infra-red to greenish yellow.

The resistance of the sulphur cell which has been described, unlike that of most selenium cells, was diminished by a rise of temperature\*. When in circuit with a Leclanché cell and a galvanometer, the effect of holding a nearly red-hot brass rod at a distance of 3 centim. from its surface, was a gradual fall of resistance, which in 15 seconds was indicated by 23 scale-divisions. When the rod was removed, the spot of light slowly returned to its original position, occupying several seconds in doing so. It is certain that the temperature of the sulphur must in this experiment have been much higher than when it was exposed to burning magnesium, with a solution of alum interposed, yet the effect was very much smaller; moreover, it was gradual instead of instantaneous.

Another experiment seems to prove conclusively that the resistance of the cell is diminished by the direct action of radiation, quite apart from any effect which may be produced by an incidental rise of temperature. On a cloudy day the cell, with the alum trough before it, was placed at a distance of 16 feet from a small window, all the other windows in the room being darkened. With the same battery and galvanometer as before, it was found that closing the window-shutter caused an instantaneous swing of the spot of light through 90 scale-divisions in the direction indicating increased resistance; and when the shutter was again opened, there was immediately an equal swing in the opposite direction. A delicate thermopile of 54 pairs, connected with an astatic reflecting-galvanometer of low resistance, was then put in the place of the sulphur cell, and the alum trough placed before the open end of the conical reflector attached to it. On opening the window-shutter, a deflection occurred indicating a current which was found by trial to be equal to that produced by the radiation of the human body at a distance of 10 ft. 6 in. It is needless to say that such a minute change of temperature as this implies was without sensible effect upon the resistance of the sulphur cell. There can then be no doubt whatever that the whole of the observed effect of the light upon the sulphur

\* This was not so with all the cells subsequently made. See description of cell no. 3 below.

was due to the action of radiation as such, any change of resistance resulting from the incidental rise of temperature being quite inappreciable.

*Cell No. 2.*—This was constructed in a somewhat different manner. A piece of silver-foil was laid upon the surface of the mica before the two wires were wound round it, and instead of having prepared sulphur spread upon one face, the whole was immersed in *pure* melted sulphur for a few minutes, and then carefully drained. Before this treatment the silver wires were of course short-circuited by the foil, but the liquid sulphur penetrated between them, forming a film of sulphide; and when cold, the resistance of the cell was about 100,000 ohms. Though this cell turned out to be somewhat less sensitive than the other, it seemed likely that, on account of its comparatively low resistance, it might be successfully used for a photophonic experiment. It was therefore connected in circuit with a battery of ten Leclanché cells and a telephone, and exposed to a rapidly interrupted beam of light. The telephone at once gave out a musical note, which was nearly as loud as that produced by a good selenium cell under similar circumstances.

The behaviour of this cell under changes of temperature was the same as that of the other.

*Cell No. 3.*—A mixture, consisting of equal parts of sublimed sulphur and precipitated sulphide of silver, was melted and spread on one surface of a slip of mica, around which two silver wires had been wound as before. No foil was used in this case. The resistance of this cell was diminished by radiation, but increased in a very marked manner by rise of temperature. A paraffin lamp, at a distance of 18 inches, produced a steady diminution of the resistance. When the lamp was placed at a distance of 10 inches, the galvanometer-needle first moved in a direction indicating a further fall of resistance; but after a few seconds, when the temperature began to rise, it turned in the opposite direction. On moving the lamp 6 inches nearer, there was at once a large deflection in the direction of increased resistance, the temperature-effect completely predominating over that of radiation.

*Cell No. 4.*—A strip of silver-leaf was attached to a glass plate by means of gold size, and the middle part of it was exposed to the vapour of boiling sulphur until both surfaces were completely blackened. The resistance of this cell was high, but for a few days it was extraordinarily sensitive, a reflected beam of sunlight instantly effecting a diminution of 80 per cent. in its resistance. About a fortnight after it was made, its sensitiveness had greatly fallen off.

All these cells resemble selenium in giving polarization-currents after being detached from the battery.

Supposing it to be true, then, that it is not in the selenium or sulphur itself, but in certain metallic selenides or sulphides, that the sensitiveness to light is resident, does it become easier to explain the phenomenon, or, rather, to deprive it of the unique position which it has hitherto appeared to hold, and assign to it a place among a class of analogous effects?

I believe that, at all events in the case of the sulphur-silver cell, it is principally at the surface of the *electrodes* that the effects of radiation are to be looked for.

If a current of electricity is passed through a mass of sulphide of silver having silver electrodes, silver will be deposited upon the cathode and sulphur upon the anode. The accumulation of silver upon the cathode will clearly produce no appreciable effect upon the conductivity of the arrangement, and need not be considered. But sulphur has an enormously high resistance, and the deposition of a mere film of free sulphur upon the anode would be sufficient to stop the current altogether. The current is not in fact stopped, because the deposited sulphur at once combines with the silver of the anode, merely adding a new layer to the electrolyte. Thus the metal of the anode gradually combines with the sulphur of the electrolyte; and the conductivity of the arrangement will depend to a great extent upon the facility with which this combination is effected, the quantity of electricity which can pass in a given time being limited by the quantity of sulphur which is capable of uniting with the electrode in the same time.

Sulphur combines with silver far more readily than with iron. If, therefore, my views are correct, we should expect a cell with an iron anode to offer a much greater resistance than one which had an anode of silver, the material of the cathode, so long as it was a good elementary conductor of electricity, being of comparatively little importance. To test this idea, a cell was made consisting of electrodes of iron and silver imbedded in a mixture of sulphide of silver and sulphur. The cell being connected with a battery and a galvanometer, the deflection was 115 divisions when the current passed from the silver to the iron through the electrolyte, and only 4 divisions when the direction of the current was from iron to silver\*. The resistance was therefore nearly 30 times as great with an

\* The resistance of the galvanometer was 3483 ohms, and it was shunted with a coil of 20 ohms. The resistance of the Leclanché cell was about 5 ohms.

iron anode as with a silver anode. It is clear that this was not the result of bad contact between the iron and the electrolyte (such as was supposed by Graham Bell in the analogous case of selenium to account for the high resistance of a cell with platinum electrodes as compared with one in which the electrodes were made of brass), because such an effect would be independent of the direction of the current. Rather it seems that the resistances of the two anodes afford data for measuring the relative facilities with which sulphur combines with silver and with iron.

Assuming it to be thus experimentally proved that the resistance of a sulphur-silver cell depends largely upon the readiness with which sulphur unites with the anode, it follows that any cause which would assist this union would at the same time diminish the resistance. Now it is well known that certain chemical combinations are accelerated by the action of radiation—the explosive union of chlorine with hydrogen under the influence of sunlight being a familiar example. The question then suggests itself, Does sulphur combine with silver more readily when exposed to radiation than it otherwise would? There is, I believe, direct evidence that it does.

A glass plate, covered with silver leaf, was placed, with the silvered side downwards, over a crucible of boiling sulphur. One half of the plate was covered with a piece of black cloth, and the arrangement was exposed to bright sunshine. In a short time the visible portion of the silver was darkened, owing to its partial conversion into sulphide; the cloth was then removed, and the silver beneath it was found to be scarcely discoloured. There was a distinct line of demarcation between the two halves. The experiment was repeated with the same result.

Since this effect might possibly have been due to other causes than the action of light (such as the unequal condensation of sulphur vapour upon the covered and uncovered portions of the plate), the experiment was made in another form. A piece of silver leaf attached to glass was brushed over with a solution of sulphur in bisulphide of carbon; and in order to keep the temperature low and uniform, the silvered glass plate was immersed in a basin containing cold water, which was placed in the sunshine. A board was laid across the top of the basin so as to shade one half of the plate, the other half being exposed to the direct rays of the sun. In a quarter of an hour the exposed portion of the silver had acquired a dark brown colour, while that which had been protected was of a pale yellow tint, the outline of the shadow of the board being sharply defined. I think we have here the strongest evidence

that the combination of sulphur with silver is assisted by radiation.

But it is not perhaps necessary to assume that the effective action of light is confined entirely to the surface of one of the electrodes. If, as is commonly believed, electrolytic conduction involves a series of decompositions and recompositions throughout the electrolyte, any cause which assists either the separation or recomposition (or both) of the components of the electrolyte might be expected to increase its conductivity; and it seems reasonable to suppose that the same influence which would assist the union of two substances when they have a tendency to unite would also be favourable to their separation when they have a tendency to separate. It is not impossible, therefore, that radiation, acting upon the surface of a thin layer of sulphide of silver through which an electric current is passing, might, by facilitating the molecular rearrangement of the atoms of sulphur and silver, exert a material influence upon the conductivity of the sulphide\*.

So far as regards the explanation of the effect of light upon the resistance of selenium, I am aware that this paper contains little more than speculative suggestions, which are at present almost entirely unsupported by experimental evidence†. It is, however, noteworthy that these speculations led to the construction of a cell which, without containing a particle of selenium, behaved almost exactly as if it were composed of that substance. How far this may be considered to prove anything with regard to selenium I do not know; but in any case the discovery of another substance possessing the same remarkable property seems in itself to be a matter of some interest.

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XXIII. *On a New Law, analogous to those known under the names Law of Avogadro and Law of Dulong and Petit.* By J. A. GROSHANS‡.

[Concluded from p. 30.]

IT may be said that, as yet, the study of the causes which influence the value of  $x$  has to be commenced, and that all that pertains to this constant is still uncertain. Still I

\* There are some experimental reasons, into which I am not at present prepared to enter, for believing that the admixture with the sulphide of a certain amount of free sulphur is necessary for the development of sensitiveness to radiation.

† It is especially desirable to ascertain experimentally whether the combination of selenium with the metals used as electrodes in selenium cells is assisted by light.

‡ Communicated by the Author. Translated by W. W. J. Nicol, M.A., D.Sc.