



XIX. The electrical properties of selenium

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XIX. *The Electrical Properties of Selenium.*
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§ 1. *Preliminary*†.

SELENIUM, which is supposed to be an elementary substance, is capable of existing in several distinct modifications. The amorphous variety consists either of a finely divided red powder, or of a vitreous mass which resembles black glass in appearance and does not conduct electricity. Amorphous selenium melts at about 100°C ., but at temperatures between 100° and 217° the black semi-liquid mass gradually hardens into a grey metallic-looking solid. This consists of Se in the crystalline form: it melts at 217° , and is a moderate conductor of electricity, its conductivity being temporarily increased by the action of light. This peculiar influence of light upon Se has attracted much attention, and below is given a list of published papers relating to the subject‡.

* Communicated by the Physical Society: read June 28, 1895.

† A summary of the principal results will be found at the end of the paper.

‡ 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; Moss, *Proc. Roy. Soc.* May 11, 1876; 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; *Proc. Nat. Acad. Sci.* April 1881; Shelford Bidwell, *Phil. Mag.* April 1881, January 1883, August 1885, March 1891; Fritts, '*Electrical Review*,' March 7, 1885, p. 208; Minchin, *Phil. Mag.* March 1891, p. 207.

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§ 2. *Selenium Cells.*

Any device consisting essentially of a mass of crystalline selenium in combination with two metallic electrodes, and so arranged as to expose a relatively large surface for light to act upon is commonly, but not very appropriately, termed a "Selenium Cell." So many inquiries have reached me as to the construction of the sensitive cells which I have at different times exhibited before this Society and elsewhere, that I venture to think a short account of the process may be usefully given here.

A slip of mica about 55 millim. long, 17 millim. wide, and 0.4 millim. thick, is sandwiched between two semi-cylinders of boxwood about 18 millim. in diameter and of somewhat greater length than the mica, the ends being held together by screws. The whole is smoothed down in a lathe until the edges of the mica are flush with the surface of the wood. A screw of 16 threads to the centim. (40 to the inch) is cut upon the middle portion of the cylinder for a length of 45 centim. The mica is then removed from the wood, and two small holes are drilled near each of its ends. An annealed copper wire 0.19 millim. in diameter (No. 36 s.w.g.) is tightly wound around the notched portion of the mica, the turns being made to occupy alternate notches, and its ends are secured by passing them through two of the drilled holes. A second wire is then wound into the other notches, its turns alternating with those of the first. These wires constitute the electrodes, and great care is taken that they do not touch each other at any point.

The next step is to apply the selenium. A brass plate 2 millim. thick is supported upon an iron tripod and covered with a sheet of thin mica; upon this is laid the prepared mica slip, small weights being placed upon its ends to steady it. The surface of the wired portion of the slip is evenly covered with 1 gramme (or a little less) of powdered vitreous selenium, and a small Bunsen burner is lighted beneath the brass plate. In a few minutes the greater part of the Se will melt: some of it, however, will probably crystallize, forming hard grey lumps, and when this occurs the heat must be continued, and if necessary increased, until all the grey lumps have disappeared. Then the Se is worked smoothly and uniformly over the slip with a steel spatula, particular care being taken that the surface is covered quite up to the edges. This operation is often found a troublesome one, but if the temperature be properly regulated, there is little difficulty about it. When the temperature is too low, hard crystalline lumps are formed; when it is too high, surface-tension causes

the selenium to gather up into drops, and it becomes as impossible to spread as if it were mercury. The Bunsen flame should be adjusted so that the temperature is only just above the melting-point, 217° ; the selenium then assumes a plastic semi-fluid condition and can be easily manipulated.

When a satisfactory surface has been secured, the cell is immediately removed by means of forceps and placed upon a thick copper plate to cool quickly. The Se surface should at this stage be black and lustrous, and the resistance between the electrodes sensibly infinite.

The Bunsen flame having been turned down sufficiently to lower the temperature to about 120° , the cell is replaced upon the hot plate. In a few minutes parts of its bright surface become dimmed, and shortly afterwards the whole turns a dull grey colour. The temperature is then cautiously raised until signs of melting just begin to appear, generally near one of the edges. When this occurs the burner is instantly withdrawn and the flame slightly lowered. The darkened spot recrystallizes in the course of a few seconds, and the burner is then replaced and left for four or five hours, during which time the temperature of the Se should be only a few degrees below the melting-point. Another hour is occupied in slowly cooling the cell, the flame being gradually lowered and finally extinguished. This process of long heating and slow cooling is generally spoken of as "annealing."

The resistance of such a cell as that described is generally from 50,000 to 100,000 ohms in the dark, and 50 or 60 per cent. less in diffused daylight. If alternately screened and exposed, it will with an electromotive force of 50 volts or upwards easily actuate an ordinary telegraph relay.

§ 3. *Hypothesis as to the Action of Light upon Selenium.*

Selenium as supplied commercially is never free from impurities, and indeed I have lately been informed by a distinguished chemist, who has given some attention to the subject, that perfectly pure selenium has not yet been obtained. Graham Bell states that the samples collected by him in different parts of the world were found to contain, among other things, the metals lead, iron, and arsenic.

Ten years ago I suggested * that metallic selenides, whether originally existing as impurities in the Se or formed at the expense of the electrodes during the process of "annealing," might play a very important part, not only in relation to the conductivity of crystalline Se, but also in bringing about the

* Proc. Phys. Soc. vol. vii. p. 129; Phil. Mag. August 1885, p. 178.

apparent change of its resistance under the influence of light. According to my hypothesis, the conductivity of Se depended mainly upon the selenides which it contained. I supposed the conduction to be of a truly electrolytic character, the current decomposing the selenides, and depositing upon the anode amorphous Se and upon the kathode the various metals. Amorphous Se is a non-conductor: unless, therefore, the deposited Se combined more or less freely with the metal of the anode, forming upon it a layer of conducting selenide, the resistance of a Se cell would, under the influence of a current, soon rise to infinity. It has been shown that Se does slowly unite with at all events some metals when merely brought into contact with them, and I ventured to suggest that light played its part in reducing the resistance by facilitating this union. The action would occur not only at the anode, but throughout the body of the Se, the recombination of the separated molecules of Se and the metal (forming the "Grotthuss chain") being similarly assisted.

This hypothesis would, as I showed, explain many observed facts which could not otherwise be readily accounted for, and I adduced in support of it several arguments which need not here be repeated. But the hypothesis postulated two important assumptions which I was not able at the time (nor when I returned to the subject five years later) to justify by experimental evidence. It assumed that solid metallic selenides conduct electrolytically, and that the combination of selenium with a metal is accelerated by the action of light.

My recent experiments, some of which are discussed in the present paper, were undertaken primarily with the object of testing these two assumptions. In the course of the investigation, however, many other interesting points presented themselves for consideration, and some of the results arrived at are also here recorded. The experiments are described in the order which appeared to be most convenient; it is of course not that in which they were actually performed.

§ 4. *The Effect of Annealing upon the Specific Resistance of Crystalline Selenium.*

The resistance of Se which has been crystallized and annealed out of contact with any metal appears to be always much greater than when metallic electrodes have been fused into it in the usual fashion. It also depends to a large extent, and in a manner which is not yet fully explained, upon the treatment which the Se has received.

Exp. 1.—A number of disks were prepared by casting Se

in a mould formed by placing a glass ring, such as is used for microscope slides, upon a glass plate. The thickness of a disk was made approximately uniform, and its surfaces polished by rubbing upon fine glass-paper laid upon a sheet of plate glass. The disk to be tested was inserted between pads of vulcanized rubber covered with tinfoil, which constituted the electrodes, and the whole was placed between hinged boards and loaded with a weight of 28 lbs. (12·7 kilos). It is unnecessary to describe the tests in detail, inasmuch as the only result arrived at was the negative one that crystalline Se has no definite specific resistance. In different tests of disks prepared from the same sample and as far as possible in the same manner, it varied from 33 megohms to 1630.

The specific resistance is certainly not always diminished, as is generally believed, by prolonged heating at a high temperature; *i. e.* between 200° and 217°. It is indeed often increased after such an operation, as in the following extreme instance.

Exp. 2.—A disk of Se was crystallized and heated for an unrecorded number of hours in a copper air-bath at about 200°. Its specific resistance was afterwards found to be 38·5 megohms. It was again heated at the same temperature for three hours. When cold its specific resistance was 660 megohms. In both cases it was cooled slowly.

§ 5. Action of Selenides.

On the other hand, prolonged heating always diminishes the resistance of a Se “cell” having electrodes fused into it. This I have attributed to the action of the conducting metallic selenide which would be formed during the heating at the expense of the wires.

Exp. 3.—For the purpose of testing this conjecture, a number of cells were constructed of Se having incorporated with it cuprous selenide in different proportions. The wire used was platinum; it was of the same gauge in all cases (0·27 millim.), and the number of turns per unit of length was also the same (10 per centim.). The surface area, however, varied somewhat, and in order to facilitate comparison the figures, as given in the annexed table, express in each case the resistance of a square centim. of surface. The light employed was always, except where otherwise stated, that derived from an 8 candle-power incandescent lamp, the filament of which was 1 ft. (about 30 centim.) distant from the face of the cell. None of the cells containing added selenide were annealed, but were cooled as soon as the Se had

crystallized. That in which there was no Cu_2Se was annealed for six hours. For comparison, the table is headed with particulars of a good ordinary copper-wire cell of similar dimensions.

TABLE I.

Composition of Cell.	Annealed or Unannealed.	Percentage of added Cu_2Se .	Resistance in dark of 1 sq. cm. Megohms.	Percentage decrease in light.
Cu Wire and Se	Well annealed	0	0.7	45 to 50
Pt Wire and Se	" "	0	13.9	33
Pt wire and Se + Cu_2Se	Unannealed.	0.5	12.0	32
" "	"	1.5	14.7	57
" "	"	3	3.6	47
" "	"	4	0.90	38
" "	"	5	0.25	28

In the cell containing 1.5 per cent. of Cu_2Se , the thickness of the Se coating was accidentally made much less than the diameter of the wires, instead of equal to it, as in the other cells: hence its unduly high apparent resistance and its correspondingly great sensitiveness (for its exposed surface was disproportionately great). In other cases the results are as regular as could be expected. They demonstrate clearly enough that a cell of fairly good sensitiveness and conductivity may be formed without any annealing, if a suitable quantity of metallic selenide be first added to the Se. They also render very evident the fact that an excessive quantity of selenide, while it reduces the resistance to a comparatively low point, only does so at the cost of the sensitiveness. This agrees with the well-known fact that an ordinary Se cell whose resistance has been unduly lowered by too long heating is only moderately sensitive to light. Exactly what part is played by the free selenium remains yet to be determined; it is certain that cuprous selenide by itself is quite insensible.

§ 6. *Sensitizing Insensitive Selenium.*

During the last fifteen years I have worked with a great many different samples of Se, and have observed that they

did not all possess exactly the same degree of sensitiveness: some were better than others, but the sensitiveness of the best was probably not more than 8 or 10 per cent. greater than that of the worst. Lately, however, I have been supplied commercially with a batch of selenium which, under the usual treatment, is almost absolutely insensitive to light. This Se differs a little in appearance from the ordinary article. In the vitreous condition its colour is of a lighter shade, and its surface is less lustrous than usual. When melted (above 217°) it forms a tenacious semi-fluid mass, which adheres like treacle to the mica and spatula and is difficult to spread; it does not exhibit the capillary effects previously referred to, and at a suitable temperature it crystallizes with great rapidity. It has not been analysed, but such impurities as it may contain probably do not include the metallic selenides commonly met with*.

Exp. 4.—Three copper-wire cells of the usual size were made with this Se and annealed for several hours. Their resistances in the dark had the abnormally high values of 170,000, 290,000, and 520,000 ohms respectively, the last named being very thinly coated. When illuminated by the incandescent lamp at 12 inches, the decrease of the resistance amounted in the case of the first two to only a fraction of 1 per cent. (instead of the customary 40 or 50 per cent.), and in the thinly-coated cell to about 6 per cent.

Exp. 5.—Two perfectly similar copper-wire cells of smaller size were coated, one with the insensitive Se and the other with ordinary Se, and annealed side by side for $5\frac{1}{2}$ hours. On subsequently testing, the resistance of the ordinary cell was found to be 20,500 ohms in the dark and 40 per cent. less when illuminated, while that of the other was 780,000 in the dark and only 2.5 per cent. less under illumination.

Exp. 6.—A cell was constructed having exactly the same dimensions as those last mentioned, and was coated with insensitive Se with which 3 per cent. of cuprous selenide had been previously incorporated. It was not annealed, but cooled gradually during about fifteen minutes. Next day its resistance in the dark was 190,000 ohms, and when illuminated by the lamp, 140,000, the decrease being 26 per cent.; in sunlight it fell to 43,000 ohms, or 77 per cent. less than in darkness.

Exp. 7.—Another cell of the same size was made in which

* Two other samples of insensitive Se have since been supplied to me from different sources.—*June 28th.*

5 per cent. of selenide was added to the insensitive Se. Its resistance in the dark was 105,000 ohms, and when illuminated by the lamp 79,000, a fall of 25 per cent.

Exp. 8.—Another similarly sized cell had 3 per cent. of lead selenide mixed with the Se. Its resistance dark was 363,000 ohms, and illuminated $10\frac{1}{2}$ per cent. less.

It appears, therefore, that the addition of a small quantity of cuprous selenide imparts a fair degree of sensitiveness to the anomalous Se, at the same time bringing down its resistance to nearly the normal value. An equal proportion of lead selenide produces a similar, though less marked effect. It would be interesting to try selenides of arsenic and other metals, but I have not yet had time to do so.

It is certain that an ordinary well “annealed” Se cell with copper electrodes contains a relatively large quantity of copper selenide. Mr. W. Hibbert was kind enough to analyse the Se taken from one of my old cells to which no foreign substance had been intentionally added, and found that it contained 2.28 per cent. of combined copper, equivalent to 3.71 per cent. of cuprous selenide. Of course this must have been derived mainly from the copper electrodes.

§ 7. *Effect of Time.*

The fact that the resistance of crystalline Se with metallic electrodes fused into it decreases very greatly in course of time was first noticed by Prof. W. G. Adams and Mr. R. E. Day*, who thought that it was due to the Se having become more completely annealed. In a former paper† I have suggested that the decrease is more probably to be attributed to the short-circuiting of the cell by an excessive amount of conducting selenide, formed by the gradual union of the Se with the metal of the electrodes. This view receives strong support from the following observations.

Exp. 9.—In the year 1891 I constructed a copper-wire cell but did not crystallize nor anneal the Se, which remained therefore in the vitreous state: its resistance was sensibly infinite. The cell was laid aside in a box until March 1895, when it was tested and its resistance found to have fallen to about 8 ohms. The cell was quite unchanged in appearance, the selenium surface being perfectly black and glossy. The decrease of resistance could not possibly be accounted for by spontaneous crystallization, and could hardly have been due to any other cause than the formation of selenide in the

* Phil. Trans. vol. clxvii. pt. i. p. 348.

† Phil. Mag. March 1891, p. 250.

interior. The cell was unfortunately destroyed before it occurred to me to use it for an experiment like the following.

Exp. 10.—A cell made in 1881 had then a resistance of about 100,000 ohms and was very sensitive to light. In 1895 its resistance had fallen to 10 ohms and it was quite insensitive. This was connected with a storage-battery of 26 cells, a detector-galvanometer being included in the circuit. When the current was turned on, the galvanometer-needle underwent a momentary strong deflexion and immediately returned to zero. The dark resistance of the cell was then found to have risen to 60,000 ohms, and it was once more sensitive to light. Clearly a short circuit caused by the selenide had been burnt out.

§ 8. *Action of Light in promoting the Formation of Selenides.*

Several attempts to ascertain whether the union of Se with a metal was assisted by illumination resulted indecisively. The following simple experiments are however, I think, fairly conclusive.

Exp. 11.—One side of a thick plate of copper was evenly coated with red amorphous Se by causing the fumes of boiling Se to play upon it. Half the plate was then covered and the other half exposed, first to diffused daylight and afterwards to sunlight. In diffused daylight the exposed half was perceptibly darkened in the course of two or three hours; in sunlight it quickly assumed a dark chocolate colour, the screened portion remaining bright red.

Exp. 12.—Two pieces of mica were similarly treated, but the exposed portions were not perceptibly darkened by prolonged exposure to sunlight. They became, however, covered with a slight "bloom," like that seen on a ripe plum, which I am inclined to attribute to the formation of an oxide.

Exp. 13.—A brass plate coated with red Se was exposed to sunlight in a photographic printing-frame under a design cut out of black paper and intended to represent a butterfly. A perfectly sharp and intense print of the design was produced upon the red Se. This was made on April 17 last: it has since been kept in the dark and is now exhibited to the Society.

The chocolate colour is closely matched by that of a mixture of red precipitated Se and cuprous selenide in about equal parts.

§ 9. *The Effect of Temperature upon the Resistance of Crystalline Selenium.*

Text-books and dictionaries of chemistry appear to be about equally divided upon the question whether the resistance of crystalline Se is increased or diminished by rise of temperature. There are high authorities for both opinions. In a paper published in 1883* I gave an account of some experiments which indicated that the resistance of Se, "or rather perhaps of selenium cells," as I was careful to add, became a maximum at a certain temperature, which varied a little with different specimens but was generally a few degrees higher than the average temperature of the air. Eight different cells were tested, showing well-defined maxima at temperatures of 13°, 14°, 22°, 23°, 23°, 24°, 25°, and 30° respectively.

On further investigating the subject I have traced this curious effect to the action of the fused-in electrodes. So far as I know from a great number of experiments, a piece of crystalline Se into which wires have been fused *always* acquires a maximum resistance at a certain temperature. On the other hand, the resistance of a piece having external electrodes pressed into contact with it is *always* diminished by a rise of temperature.

Exp. 14.—A rectangular plate of Se was cast in one of the white-glazed earthenware "pans" in which moist water-colours are sold. Two platinum wires were made red-hot, and their ends embedded along the shorter sides of the rectangular plate a little below the surface. The plate was then crystallized and annealed and its surfaces smoothed with glass-paper.

The plate was suspended inside an air-bath, the bulb of a thermometer being in contact with it, and the resistance between the platinum-wire electrodes was taken at temperatures ranging from -2° to 12° . The results, which are given in the second column of Table II., indicate that the resistance was greatest when the temperature was 6° .

The same plate was then placed between two pads of india-rubber covered with tinfoil which served as electrodes, and were pressed into good contact by a weight of 500 grammes. The arrangement was placed in the air-bath, and the resistance between the opposite faces of the plate observed at various temperatures. As is shown in the third column of Table II., the resistance diminished steadily as the temperature rose.

* Phil. Mag. Jan. 1883, p. 31.

TABLE II.

Temperature. Degrees C.	Resistance between Electrodes fused into ends. Megohms.	Resistance between Electrodes pressed against surface. Megohms.
- 2	45.6	
0	48.7	
2	52.0	38.5
4	52.3	36.8
6	53.3*	34.0
8	52.5	30.2
10	49.6	26.6
12	46.7	23.9

* Maximum.

Thus with rising temperature the resistance of the *same* piece of Se appears to reach a maximum when measured between fused-in wires, and to decrease *ab initio* when measured between electrodes which are pressed upon its surface.

Beyond doubt the resistance of the Se really falls in both cases. The apparent preliminary rise when the electrodes are fused in, is due to the unequal heat expansion of the Se and of the metal. The coefficient of linear expansion of Se is twice as great as that of copper and three times as great as that of platinum. The effect of heating is to loosen the tight grip of the Se upon the metal and so to increase the resistance of the junction. The rate at which this junction-resistance increases is at first greater than that at which the specific resistance of the Se diminishes: soon, however, the latter effect predominates, and thus the resistance of the combination of Se and a metal passes a maximum.

§ 10. Porosity of Crystalline Selenium.

The consideration of certain phenomena, which will be referred to later, led me to believe that crystalline Se, notwithstanding its metallic appearance, must be a sensibly porous substance. Experiments were made with the view of ascertaining whether this was the fact.

Exp. 15.—One end of a brass tube was closed by a polished disk of crystalline selenium, 11.2 millim. in diameter and 1.25 millim. thick, which was tightly fixed by an indiarubber collar: to the other end was attached a glass tube which terminated in an open point about 3 millim. in diameter. The whole of the indiarubber and the edges of the Se disk were thickly coated with shellac varnish. The closed end of the tube was dipped into water and air was forced into the open end. No bubbles were formed upon the Se: if therefore Se be porous its pores must be very small.

Exp. 16.—A transpiration experiment was then made. The tube was fixed in an upright position with the Se disk at the top and the glass point at the bottom, the latter dipping into a basin of water. A wide-mouthed glass bottle was supported mouth downwards over the tube, enclosing its upper end. Coal-gas was slowly admitted into the bottle from a small nozzle. The indiarubber tube conveying the gas was for seven feet (about 2 metres) of its length coiled up in a vessel of cold water. When the gas was first admitted water rose for a short distance inside the glass tube owing to the cooling effect of the refrigerated gas: but after a minute or two it began to descend again, and soon air-bubbles were slowly but regularly given off at the pointed end. This continued until the bottle of gas was removed, when the bubbles at once ceased and the water again began to rise in the tube.

Crystalline Se is therefore sensibly porous, and no doubt absorbs moisture from the air.

§ 11. *The Polarization of Selenium by Currents.*

Among the many remarkable properties of Se which were first observed by Prof. W. G. Adams and Mr. R. E. Day in their well-known research, is the power it possesses of setting up a secondary or polarization current after being disconnected from a battery. As all who have worked much with Se must know, the opposing and ever varying electromotive force of polarization renders it very troublesome to make accurate resistance tests by the ordinary bridge method. Unless it is worth while to expend a considerable amount of time, one has to be contented with two or at most three significant figures, and even this degree of accuracy cannot be attained unless care is taken to depress the battery and galvanometer keys only for a moment*.

* If the battery key be kept down for a few seconds, and after it is raised the galvanometer key be depressed, a considerable deflexion due to the secondary current will generally be observed. For exact measurements it is necessary to balance to a constantly changing false zero.

In a former communication I stated my belief that these polarization effects resulted from the electrolysis of the metallic selenides contained as impurities in the Se. Whether this be so or not, the following experiments plainly indicate that the presence of moisture is necessary for the production of the phenomenon.

Exp. 17.—The electrodes of a Se cell were connected first with the poles of a battery, and then by means of a “change-over” switch with a galvanometer: this produced a deflexion of 90 divisions, indicating an E.M.F. of rather more than $\frac{1}{100}$ volt. The cell was then placed in a glass receiver over strong sulphuric acid, the connecting wires being passed through an indiarubber stopper. From time to time it was successively joined to the battery and the galvanometer, and the polarization current was observed to be gradually diminishing. After 18 hours the deflexion was only 3 divisions. The air was then exhausted from the receiver, and 24 hours later no polarization current whatever could be detected, even after prolonged connexion with the battery. A current greater than $\frac{1}{300}$ part of that which occurred in ordinary air would certainly not have escaped observation.

Exp. 18.—The cell was afterwards suspended for an hour in a receiver over a basin of water and then tested for polarization. The spot of light was immediately deflected far beyond the limits of the scale.

Probably therefore the polarization results merely from the electrolysis of water; in any case the presence of water seems to be requisite for its production.

It is perhaps worth noting that little if any polarization is exhibited by crystalline Se of the coarsely granular form obtained by gradually *lowering* the temperature of the molten substance, instead of by heating solid vitreous Se. The specific resistance of this form is much lower than that of the other, and its sensitiveness is also less.

§ 12. *The Effect of Moisture upon Conductivity and Sensitiveness.*

The water ordinarily present in Se, even if it had no other effect, would naturally influence its apparent conductivity by acting as a shunt or alternative path for the passage of the current. We should expect, therefore, that if a cell were made as dry as possible, its resistance would be increased, and this was found to be the case.

Exp. 19.—A cell with a Se surface measuring 4 centim. by 1.5 centim., and containing 64 turns of 0.19 millim. copper wire, was suspended in a receiver over sulphuric acid, and tests

were made of its resistance both in darkness and under illumination by an 8 candle-power lamp at 30 centim. The results are given in Table III.

TABLE III.
Selenium Cell in Receiver over H_2SO_4 .

Time. Hours.	Resistance. Dark.	Resistance. Illuminated.	Percentage Decrease.
0	50,400	25,400	49.5
28	83,000	35,500	57.2

The dark resistance of the cell, it will be seen, increased in 28 hours from 50,400 to 83,000 ohms : if, therefore, the water which it originally contained acted like a metallic shunt, its resistance taken alone must have been about 128,000 ohms. Now it was found that a thin plate of Se, after having been dried over sulphuric acid for 22 hours, lost $\frac{1}{2800}$ part of its weight. The weight of the Se in the cell used in the present experiment was about 0.4 gramme ; probably, therefore, it originally contained about $\frac{1}{7000}$ gramme of water. Knowing the dimensions of the cell (which are given above), it is easily calculated that if this quantity of water when uniformly distributed between the electrodes of the cell offered a resistance of 128,000 ohms, its specific resistance must have been approximately 7800 ohms. This is of the same order of magnitude as the specific resistance of good distilled water, though that of purer water is of course much higher. We may fairly conclude, then, that absorbed moisture plays no active part in diminishing the dark resistance of Se, but behaves merely as if it were an inert shunt.

As regards *sensitiveness*, moisture might conceivably exert one of four different influences. If it acted simply as a shunt, its removal ought to increase the sensitiveness of the cell in an easily calculable degree. If its presence were essential to the chemical or physical change which is effected by the agency of light, then a perfectly dry cell would also be perfectly insensitive. If moisture, without being indispensable, were yet in some degree favourable to the operation of light, the sensitiveness of the cell, though it might possibly be increased when the water was withdrawn, would still not be so great as if a metallic shunt of equal resistance had been cut out. Lastly, if the influence of

water were positively prejudicial, its removal would result in a greater increase of sensitiveness than if it had been a mere shunt.

The figures in Table III. seem to show that the presence of water, though not essential to sensitiveness, does to some extent assist the action of light. The percentage decrease of the resistance of the dried Se under illumination is considerably greater than that of the undried, but still it is not so great as it would have been if a shunt of 128,000 ohms (the resistance of the water alone) had been withdrawn. In the latter case the resistance of the dry cell in the light would have been only 31,700 ohms instead of 35,000, and the percentage decrease 61·8 instead of 57·2.

Exp. 20.—Three cells were at different times constructed, and after being kept for some hours at a temperature of about 200° were without any previous cooling transferred as rapidly as possible to the sulphuric acid receiver. All turned out to be sensitive to light while in the dry air. Unless, therefore, Se can condense moisture in its pores at a temperature of 200°, which is not probable, its sensitiveness to light is not entirely dependent upon the presence of water. Having regard to the observations detailed in the next section this was contrary to my expectation.

§ 13. *Attempted Electrolysis of Metallic Selenide.*

Many abortive attempts were made to ascertain whether cuprous selenide conducts electricity entirely like a metal, as is generally believed, or like an electrolyte, as required by my hypothesis. The experiments of which an account is given in this section appear to show that if the conduction is not altogether electrolytic, it is under certain conditions, at least partly so. It must, however, be admitted that the results, though of considerable interest, cannot be regarded as conclusive. The condition requisite for apparent electrolysis is that the surface of the selenide should be moist, a condition of course suggestive of some secondary action.

Exp. 21.—A mass of cuprous selenide about 2 millim. in thickness was placed between two platinum foil electrodes, each of which was covered with four layers of filter-paper moistened with distilled water. The arrangement was pressed together by a weight of 28 lbs. (12·7 kilos), ordinary precautions being taken to avoid short-circuiting. A current averaging 0·03 ampere was passed through the moist selenide for about four hours. On examining the papers afterwards, it was found that those which had been in immediate contact with the selenide were stained a dark grey colour, due

evidently only to transferred particles of selenide. The other papers had received stains which differed greatly in appearance according as they were upon the anode or the kathode.

On the *anode* papers the stains were scarlet, and I satisfied myself that they were beyond doubt due to red amorphous Se. For (1) stains of a precisely similar hue and character were obtained by electrolysing a solution of selenious oxide contained in a pad of filter-paper, though of course in this case the stain appeared upon the kathode. (2) The stains turned dark brown when heated. (3) They were not affected by cold hydrochloric acid, as red oxide of copper would have been. (4) Nor by sulphuric acid. (5) Nor (unless very slowly) by cold nitric acid. (6) Hot nitric acid quickly dissipated them. (7) So also did a mixture of cold nitric and hydrochloric acids. (8) The red stuff could be volatilized at a temperature below that at which the paper was scorched.

On the *kathode* papers the stains were of a dark brown, nearly black, shade, surrounded by small irregular patches of green, blue, and orange. The dark-brown stuff acquired a metallic copper-coloured lustre when burnished, which is sufficient proof that it consisted, largely at all events, of finely divided metallic copper. It was ascertained that if a little of the selenide itself were finely powdered, rubbed into moist paper and dried, no such metallic appearance was produced by burnishing.

The experiment was repeated several times with variations in the details : *e. g.* in one case the selenide was fused with an excess of Se, in another with an excess of Cu. But it was invariably found that red stains were formed at the anode, and almost invariably traces of metallic copper appeared at the kathode.

This experiment naturally led me to try to obtain electrically liberated selenium in larger and measurable quantities.

Exp. 22.—Some selenide of copper was prepared by heating together 126 parts of shredded copper-foil and 79 of crushed Se in a closed crucible to bright redness. The product was an iron-grey, cindery-looking mass.

A fragment of this was held in a brass clip, and the lower portion of it dipped into a beaker of water opposite a strip of Pt foil. The selenide was joined to the negative pole of the battery, the Pt to the positive : thus the water was made the anode in relation to the selenide. A current of 0.025 ampere was passed for half an hour. In a few minutes after starting, the water had become scarlet and quite opaque with suspended red Se. Unfortunately, however, the selenide was very friable, and numerous small particles were detached from its

surface by the hydrogen bubbles which formed upon it; these became mixed with the liberated Se and made it impossible to ascertain the weight of the latter.

Exp. 23.—In order to obtain a more coherent substance, two parts of Se were thoroughly incorporated with one of Cu_2Se ; the mixture was then fused in an earthenware mould, and thus formed into a rectangular plate weighing 1·0731 gramme. Se itself being a very bad conductor, it was believed that practically the whole conduction would take place through the selenide. The plate was immersed in water with a strip of Pt, and a current averaging 0·023 ampere was passed for ten minutes. As soon as the circuit was closed the black plate began to give off dense red clouds; and when it was dried and weighed after the experiment, it was found to have lost 0·0250 gramme. If the decomposition had been primarily electrolytic, the weight of liberated Se, assuming its electrochemical equivalent to be 0·00082 *, would have been no more than about half that amount, namely 0·0113 gramme. The red Se was filtered out of the water and examined for particles of *débris*. None were detected by the unassisted eye, but under the microscope many became visible, though whether in sufficient quantity to account for the observed excess of weight is somewhat doubtful.

Exp. 24.—This was a repetition of the last, except that the plate contained six parts of Se to one of Cu_2Se (instead of two to one) and weighed 1·0223 gramme. The current, which averaged 0·016 ampere, was left on for 30 minutes. The actual loss of weight was 0·0386 gramme; the calculated loss, according to the electrolytic law, being 0·0236 gramme. In this case, therefore, with a weaker current and a less friable mixture, the observed exceeded the calculated loss by only 64 per cent. instead of 121 per cent. as in the previous instance. The microscope again revealed the presence of numerous small black particles. The closer approximation is in favour of the possibility that the excess might have been due to the disruption of fragments of the selenide. Further experiments, which need not be detailed, leave the point still doubtful.

This effect of electrical action may be exhibited in a striking manner as follows :—A sheet of moistened filter-paper is laid upon a metallic plate, preferably of Pt, which is in connexion with the positive terminal of a 50-volt battery; a pencil formed of one part of Cu_2Se and six parts of Se is connected

* The electrochemical equivalent of hydrogen multiplied by the atomic weight of Se = $0\cdot000010384 \times 79 = 0\cdot000820336$. Quite possibly, however, the E.C.E. of Se is only half this value.

by a flexible wire to the negative terminal. When this black pencil is drawn over the paper, it makes a bright red mark which is immediately broken off if the current is interrupted or reversed. If a copper plate be used, the marks will be brown instead of red.

The red stuff separated in the foregoing experiments turned black when heated, and fused and crystallized like ordinary Se. The resistance of a small cell made from a portion of it was 65 per cent. lower than the average; the cell was very sensitive to light, the diminution of its resistance under illumination being 53 per cent.

The question naturally presented itself, whether the separation of the red Se might not in some not easily imagined manner be due to the hydrogen liberated from the water, and not primarily to the current.

Exp. 25.—To test this a zinc wire 1·7 millim. in diameter was coated with a fused mixture of Se and Cu_2Se and immersed in dilute sulphuric acid. The acid penetrated the pores of the coating, and soon small bubbles of hydrogen began to rise from the surface, continuing for about 5 hours. The coating was then broken up, and it was found that all the zinc inside it had been dissolved. A microscopic examination of the fragments failed to disclose the smallest trace of any red Se.

The experiment was repeated with the substitution of ordinary commercial Se, and the same negative result was arrived at. It was ascertained that sulphuric acid did not dissolve the red stuff.

Exp. 26.—An experiment was arranged with the view of determining whether the current exerted any action, real or apparent, upon Se itself when unmixed with any metallic selenide except such as it might contain as an accidental impurity.

A well-annealed plate of crystalline Se having a Pt electrode fused into one edge was supported in water, the electrode being about 5 millim. above the surface. A slip of Pt foil was also immersed, and the two were joined respectively to the terminals of a storage-battery of 26 cells. Until the current had been passing for more than 24 hours, there was no perceptible discoloration of the water. Shortly afterwards it was found that the plate was surrounded by a slight red deposit just above the water-line, and that the lower part of the water had become pink. On examination, it appeared that the red stuff proceeded entirely from a small hole in the plate above the water-line: the Se was therefore broken up and the course of the hole, which was full of water, was

traced and found to terminate very near the Pt electrode, where no doubt platinous selenide existed.

This experiment, though not conclusive, tends to show that Se unmixed with selenide is not acted upon by the current. It is possible that moist crystalline Se may be converted into the red amorphous form by electrical action, but the question cannot be definitely settled until perfectly pure Se is obtainable.

§ 14. Photoelectric Currents.

Another of the interesting discoveries of Adams and Day was the fact that an electromotive force could be set up, and a current started in annealed Se merely by the action of light*. This observation has been fully confirmed by subsequent experimenters, and the belief has been expressed that the phenomenon affords an example of the direct conversion of the energy of light into that of electricity. Others have held the opinion that the effect is of a purely thermoelectric nature. My own investigations have led me to the following conclusions:—

(1) The effect is undoubtedly due to light and not to heat; or, more accurately, it is brought about by the action of radiation, and not by change of temperature.

(2) The energy of the photo-electric current is primarily of chemical or voltaic origin, and is not derived from radiation. Light merely has the effect of facilitating the chemical process, and can have no further influence when the supply of unused material is exhausted.

Exp. 27.—A rectangular plate of Se measuring $14 \times 11 \times 2$ millim. had Pt wire electrodes fused into its two ends and was "annealed" for several hours. The electrodes being connected with a galvanometer, a piece of magnesium ribbon was burnt near the Se: a deflexion immediately occurred showing a current which ceased as soon as the light was extinguished. By screening the two ends alternately, it was ascertained that the effect was produced only at one junction, the other being quite insensitive. (It may happen in different cases that both junctions are sensitive or neither. As will be shown later, sensitiveness points to imperfect electrical contact between the Se and Pt due perhaps to a film of red Se.) The direction of the current through the sensitive end was from Se to Pt.

The Se plate was afterwards placed under a glass receiver with a basin of water, and connected with the galvanometer by wires passing through a caoutchouc stopper. In a minute

* *L. c.* p. 333.

or so a small current was indicated which, after slowly increasing for about 15 minutes, became constant. While magnesium was being burnt near the receiver, the strength of the current was greatly intensified; even diffused daylight temporarily increased the deflexion to the extent of 150 scale-divisions. The direction of the current was as before from Se to Pt.

The plate was then enclosed in a receiver over sulphuric acid. In 8 minutes the permanent current had completely disappeared, and exposure to diffused daylight caused a deflexion of only 2 divisions. In 20 minutes burning magnesium at a distance of 6 inches failed to produce any effect whatever. The Se had completely lost its power of generating a current under the influence of light.

The natural inference seems to be that Se (or Se containing selenide) is slowly oxidized by water, and that the oxidation is increased by the action of light*. Some points bearing on the question will be further considered in the next section.

§ 15. *The Thermoelectric Quality of Annealed Selenium.*

Adams and Day believed they had obtained evidence that the thermo-electric quality of crystalline Se was altered by prolonged annealing. To use the old-fashioned terminology, they thought that by the process of annealing Se was raised from its place at the bottom of the thermo-electric series, which the experiments of Matthiessen had assigned to it, to a position somewhere above that of platinum. In other words, if a Se-Pt junction were heated to a temperature slightly above that of the other junctions in the circuit (the latter being at the ordinary temperature of the air), then, if the Se were crystallized but not thoroughly annealed, there would be a current from Pt to Se through the heated junction, but if the Se were well annealed the thermo-current would be in the reverse direction—from Se to Pt.

They applied heat at a junction by directing upon it a blast of hot air from a glass tube terminating in a fine nozzle, the tube being heated over one or more Bunsen burners. Where it was possible, heat was also applied by holding the junction

* Later experiments render this doubtful. With Se which does not contain any considerable admixture of Pt_2Se (and perhaps it should be added, which has not been previously used as an anode) the photo-electromotive force appears to be always in the *opposite* direction—from Pt to Se. And this seems to be the case not only with water as the electrolyte, but also with the other badly conducting liquids, such as cenanthol, used by Prof. Minchin.—*June 28th.*

of Pt and Se between the finger and thumb. All the pieces of Se with which they worked had had Pt wires fused into their ends before being annealed.

The following experiments point to a conclusion different from that of Adams and Day.

Exp. 28.—Experiments were made with three different specimens of Se, all of which had been annealed for many hours. None of these had electrodes fused into them. The arrangements were varied in details, and the Pt-Se junctions heated in different ways. In all cases the direction of the thermo-electromotive force was from Pt to Se across the hot junction. The direction of the current was not affected by the addition of platinous selenide to the Se.

Further experiments were made with the Se plate referred to in the preceding section which had Pt wires fused into its ends.

Exp. 29.—The Pt wires being connected with the galvanometer, it was found that when one junction was touched with the finger there was as usual a current from Pt to Se, but that when the other was touched (that which had generated the photo-electric currents in a former experiment) there followed a current in the opposite direction—from Se to Pt.

All the following observations were made with this anomalous junction.

Exp. 30.—The junction was heated by touching it first with the pointed tip of a warmed glass rod and afterwards with a hot copper wire. In both cases there resulted a current in the *normal* direction—Pt to Se.

Exp. 31.—A bent glass tube having a fine nozzle at one end was heated over a Bunsen flame, and air was blown through it from the mouth upon the junction. Result, an *abnormal* current—Se to Pt.

Exp. 32.—The last experiment was repeated, but the air was driven through the tube by a foot-blower. Result, *normal*—Pt to Se.

Exp. 33.—The tube was allowed to cool, and when quite cold air from the lungs was again blown through it. Result, a current from Se to Pt stronger than that obtained with the hot blast in *Exp. 31*.

Exp. 34.—A small piece of sponge moistened with tepid water was held upon the end of a wire near the junction but not touching it. There immediately followed a small current from Se to Pt.

In short, the anomalous current from Se to Pt was in every case clearly started, not by heat but by moisture.

The succeeding experiments indicate that at the anomalous junction the electrical contact between the Pt and Se was imperfect, and that the Se contained a certain amount of platinous selenide.

Exp. 35.—One part of platinous selenide having been incorporated with six parts of Se, the mixture was fused and crystallized. Thus was obtained a button of crystalline Se containing about 15 per cent. of platinous selenide. The button and a piece of Pt foil were partly immersed in water and their dry ends connected to the galvanometer. A voltaic current was indicated from the button to Pt through the water.

Exp. 36.—The button was dried and tested for a thermo-current with Pt. Result, current from Pt to button through the junction. The button, therefore, behaved thermo-electrically like ordinary Se.

Exp. 37.—By means of an adjustable spring a strip of Pt foil was arranged so as to press lightly on the button. The two were connected with the galvanometer.

Touching the button near the junction with a hot wire caused a current from Pt to button.

Holding the tip of the finger very near the junction without actual contact caused a current from button to Pt.

Blowing air upon the junction from a hot glass tube produced a current from Pt to button when the air-blast was derived from a foot-blower, and from button to Pt when air from the lungs was blown through the hot tube.

Thus all the thermo-effects of the "anomalous" junction were completely imitated. Perhaps in the case of that junction good contact was prevented by a film of non-conducting red Se, or possibly the wire electrode may have been simply loose.

These effects could not be produced when using a button which consisted of Se annealed without contact with a metal and containing no added selenide, the voltaic effect being then similar in direction to the heat-effect.

Summary.

1. The conductivity of crystalline Se appears to depend principally upon the impurities which it contains in the form of metallic selenides. It is suggested that the selenides conduct electrolytically, and that the influence of light in increasing the conductivity is to be attributed to its property of facilitating the combination of selenium with metals in contact with it.

2. The specific resistance of crystalline Se has no definite value but is always very high, varying in the specimens tested from about 30 to 1600 megohms. It is not in general diminished by prolonged heating unless the Se is in contact with a metal (Exps. 1, 2).

3. A Se cell having Pt electrodes and made with Se to which about 3 per cent. of cuprous selenide has been added, is, even though unannealed, greatly superior both in conductivity and sensitiveness to a similar cell made with ordinary Se and annealed for several hours. It is not, however, quite equal to a cell prepared in the usual way with copper electrodes (Exp. 3).

4. A particular sample of commercial Se which, when treated in the ordinary manner, was almost absolutely insensitive to light, was rendered sensitive by the addition of a little metallic selenide (Exps. 4-8).

5. The great fall of resistance exhibited by pieces of Se with fused-in electrodes after the lapse of a few years, is not due to any material lowering of the specific resistance of the Se, but to short-circuiting by selenide formed at the expense of the electrodes. The resistance of an old cell was instantly raised from 10 ohms to 60,000 by connecting it with a 52-volt battery and thus burning out the short circuit (Exps. 9, 10).

6. Red Se in contact with copper or brass is quickly darkened by the action of light, owing, it is suggested, to the formation of selenide. Photographs may be printed on copper or brass coated with red Se and preserved in darkness for a long time (Exps. 11-13).

7. The resistance of crystalline Se always decreases with rise of temperature. The apparent increase of resistance on heating generally observed when the electrodes are fused into the substance, is to be explained by the fact that the heat-expansion of the Se is much greater than that of the metallic electrodes; imperfect contact is consequently produced at the junction (Exp. 14).

8. Crystalline selenium is porous and absorbs moisture from the air (Exps. 15, 16).

9. The polarization of Se after being traversed by a current is due to absorbed moisture (Exps. 17, 18).

10. The moisture ordinarily present in Se renders the apparent resistance much lower than the true resistance of the substance (Exp. 19).

11. The presence of moisture is not essential to sensitiveness, but appears to be in a slight degree favourable to it (Exps. 19, 20).

12. When a current is passed through cuprous selenide between platinum electrodes which are covered with moistened paper, red Se is deposited on the anode paper and metallic copper on the kathode paper (Exp. 21).

13. If cuprous selenide is made the kathode and a strip of Pt the anode in water, red Se mixed with detached particles of the selenide is deposited in the water (Exp. 22).

14. With a mixture of cuprous selenide and Se the quantity of detached black particles is greatly diminished, but the weight of the separated red Se appears to be greater than that required by the law of electrolytic decomposition. Possibly the current has the effect of converting pure crystalline Se when moistened into the red amorphous variety (Exps. 23, 24).

15. The hydrogen produced by the action of zinc upon dilute sulphuric acid has no effect upon the cuprous selenide nor upon Se in contact with the zinc (Exps. 25, 26).

16. The photo-electric currents sometimes set up when light falls upon Se are dependent upon the presence of moisture and are no doubt of voltaic or chemical origin. (Exp. 27).

17. Experiments which have seemed to place well-annealed selenium above platinum in the thermo-electric series were vitiated by the presence of moisture. Dry Se is always below Pt (Exps. 28-37).

XX. *The Measurement of Varying Currents in Inductive Circuits.* By ALFRED W. PORTER, B.Sc., *Demonstrator of Physics, University College, London,* and DAVID K. MORRIS, *1851 Exhibition Scholar, University College, London* *.

THE following paper describes an application of the principle of the potentiometer to the measurements of rapidly varying (but not alternating) differences of potential; and hence, to the measurement of the currents to which they give rise: a problem which presented itself in the course of an investigation into the propagation of magnetic induction in iron which was begun more than a year ago. This investigation we hope shortly to publish.

A non-inductive resistance r (fig. 1) is connected in series with a magnetizing coil the current in which we desired to measure; so that the potential difference between the terminals of r is at any instant a measure of the current in the coil. When the current is steady, this difference of potential can

* Communicated by the Authors.