ART. LII.—*On a New Form of Selenium Cell, and some Electrical Discoveries made by its use;* by CHARLES E. FRITTS, of New York City.

IN the following pages I give, in a condensed form, the chief results brought out in a paper presented by me to the American Association for the Advancement of Science, at the meeting at Minneapolis in August last.

The new form of selenium cell which I have devised has the following features:

1st. Its resistance can readily be made as low as desired. Some cells have been made having a resistance as low as nine ohms. But I have generally used those measuring between 500 and 5,000 ohms.

2d. The light is caused to strike the cell in the same plane or general direction as the current.

3d. They are made in any form to be easily handled and used, and are practical working apparatus, both for scientific researches and technical uses. The cost, when completed, is ordinarily about $100 each.

4th. They are far more sensitive to light than any before known. One cell was cited which had fifteen times as high resistance in dark as in ordinary diffused daylight in a room.

5th. They exhibit other properties in an equally high degree, as specified in the paper.

The process of purifying the selenium was first explained, resulting in the separation of the product into a number of portions, having very perceptible differences of behavior, both in melting and annealing. One portion would become soft while held in the hand, and could not be made to anneal properly at any temperature, while another portion would anneal and become hard at a low heat and could not be melted without previously going through the annealing process. Yet both are supposed to be absolutely chemically pure selenium. The conclusion is that commercial selenium is a mixture, consisting of several distinct portions, which must either be different allotropic forms of the element, or new elements, similar in appearance, chemical reactions and physical properties, yet distinctly different in many respects.

I have found the "vitreous" form, or quickly cooled selenium, to have many different colors even from the same small piece of the chemically pure substance,—varying from very dark brown, almost black, through shades of brown, blue, purple, and violet, to a beautiful rose-red hue. These are distinct from the magnificent ruby-red color which vitreous selenium shows when a very thin sheet of it is viewed by transmitted light. The granular or crystalline form also varies,—being

sometimes of a very light lead color, at others a very dark gray, a violet, a purple, a dull gold color, and occasionally a blue. These colors are caused by heat.

I have tried many different metals and substances as bases for selenium cells, including iron, brass, copper, zinc, tin, lead, platinum, silver, gold, nickel, german silver, aluminum, bismuth, carbon, wood, mica and glass. My preference is for brass, zinc, or iron or copper thinly coated with tin.

Descriptions were given of cells of the forms previously known, especially of the "strip" cell, made for comparative tests with my own form. The sensitiveness to light of cells heretofore made has usually been quite low—one whose resistance would fall to one-half, or 50 per cent change, by exposure to sunlight, was uncommonly good. Probably the average of results would not exceed 10 per cent of change from dark to light. The most sensitive selenium cell on record up to this time was that of Dr. Werner Siemens, which was stated to have a resistance in dark 14·8 times as great as in sunlight. His measurements of this cell are given in table A, annexed hereto. Table B gives several measurements of a cell of my form, and the paper also gave the measurements of a number of other cells of my construction to show their extreme sensitiveness to light.* A lot of my cells, five in number, presented

* I have just been measuring a new series of selenium cells of my form and find several of them far more sensitive to light than any of those mentioned in my paper before the American Association for the Advancement of Science. Their sensitiveness is so extraordinary that I hasten to put them on record. Brass cell No. 24, measured Sept. 4th, showed twenty-five times the conductivity in sunlight that it had in the dark, and brass cell No. 23, showed about thirty times as much,—the exact ratio being 29·63 to 1.

I have measured the same cells again to-day, together with several others, with the results given in the following table. All the cells were measured "gold anode," i. e., with the current entering the cell at the gold electrode, and with 23 elements of Leclanché battery, except Nos. 22, 23 and 8. The time was between 2 and 4 P. M., sky partly cloudy, sunlight good but not first-rate.

TESTS OF SELENIUM CELLS IN LIGHT AND DARK.

Selenium cell.	Battery.	In dark.	Sunlight.	Ratio.	Date.
No. 24.	23 cells.	32,500 ohms.	1,300 ohms.	25· to 1	Sept. 4, 1883.
24.	23 "	48,500 "	1,100 "	44·09 to 1	" 5, "
23.	10 "	1,600 "	54 "	29·63 to 1	" 4, "
23.	10 "	1,510 "	50 "	30·2 to 1	" 5, "
25.	23 "	15,000 "	750 "	20· to 1	" " "
22.	23 "	1,530 "	80 "	19·12 to 1	" " "
22.	10 "	2,030 "	130 "	15·6 to 1	" " "
6.	23 "	5,040 "	170 "	29·65 to 1	" " "
5.	23 "	2,400 "	150 "	16· to 1	" " "
10.	23 "	60,000 "	3,600 "	16·6 to 1	" " "
17.	23 "	1,790 "	250 "	7·1 to 1	" " "
8.	10 "	30,000 "	1,000 "	30· to 1	" " "

I have a number of others not yet tried, which may give even greater results. But is it not astonishing that the electrical resistance of a substance should be

for inspection and trial by the members of the association, was then described.

As the result of some thousands of tests and measurements made by me, I have reached the following new conclusions:

1st. The electrical resistance of a cell changes enormously with different battery powers. There does not appear to be any invariable law governing this change, but each cell seems to have its individual character in this respect. In most cases the resistance becomes lower as the electromotive force of the current increases. One cell cited measured, with one Leclanché element, 14,000 ohms; with 5 elements, 9,900 ohms; with 10 elements, 7,600 ohms; with 23 elements, 4,600 ohms. Another measured, with 23 elements, 3,600 ohms; with 10 elements, 8,000 ohms; with 5 elements, 10,000 ohms. In other cases, but less frequently, the resistance increases as the battery power increases. These changes may be produced in either direction, and as often as desired.*

2d. I have discovered that simply reversing the direction of the current through a cell can make its resistance, in some cases, as much as ten or fifteen times as high as before, even though that increase should amount to millions of ohms. In some instances the change may be even greater, in others not so much, but it is seldom less than twice as much, or as two to one. When the original direction of the current is restored, the resistance also returns, and these effects can be repeated any number of times. The cell is sensitive to light in both cases, but is generally more sensitive when the current enters the selenium at the same surface which the light is acting upon. Instances of such changes were given, and several hypotheses were considered, but none were thought to satisfactorily account for this phenomenon.†

forty-four times as much in the dark as in the sunlight? I also wish to record the fact that I have constructed a selenium cell whose resistance becomes greater in the light and less in the dark,—being, so far as I know, the first instance of that kind ever obtained.—New York, Sept. 5th, 1883.

* In rare instances, the increase of resistance goes on up to a certain battery power, and any further increase of intensity in the current causes a fall in the resistance,—so that a change from that battery power in either direction would produce the same change in the resistance of the cell.

† The foregoing changes are not always in the same direction. That is to say, if the cell has a certain resistance, with the positive pole of the battery connected to a certain electrode of the cell, the resistance will in some cases be increased by connecting the negative pole of the battery to that electrode, and in other cases it will be lowered. Instances have been found where reversing the direction of the current caused no change in the resistance of the cell. And, what is still more singular, I have had two cells which reversed their action while being experimented with,—so that the electrode which offered the highest resistance to the positive current at first, afterwards offered the lower resistance to it, no change having been made in the connections or conditions. The selenium or the cell seemed to have been in some way permanently affected by the action of the current flowing through it. The cause of this change has not been ascertained.

After some speculations as to whether the foregoing actions are properties of selenium, or are produced by the arrangement of selenium in contact with substances so widely separated from it in the electrical scale, I observed that it is at least evident that the peculiar construction of my cells causes these actions to be manifested many times more powerfully by them than by cells of other forms, and then inquired: If it be possible, by such simple means as are employed in my cells, to obtain these results, may not means be found to still further facilitate these manifestations, and so intensify and exaggerate the results,—and even to obtain others yet unthought of, and possibly still more surprising?

3d. Still I have found that the *kind* of battery employed has a great deal to do with the performance of the cell. Take iron cell No. 1 as exemplifying this. This plate is one of the best, having given a change of 83 per cent, has been used in almost every conceivable way, and always proved good. Yet on removing the Leclanché battery which was usually employed, and substituting the small bichromate plunge battery, this plate became apparently sulky, and finally refused to respond at all to the action of light. Changing from 24 cells to 48 cells of battery has but little effect, whether the gold is the anode or cathode. It is still absolutely insensitive to light.

But on changing the battery to 96 cells its resistance jumps from 265 ohms to 11,500 in dark and 5,000 ohms in light, resuming its old sensitiveness, but apparently under compulsion. On changing to gold cathode, it sinks from 9,000 to 1,750 ohms in dark, then gradually falls to 275 in the dark, and the same in the light. Reversal to gold anode produces no change; it still remains at 275, sinks to 250 dark, and 245 light, and, had another measurement been taken, would doubtless have proved insensitive again. On removing the obnoxious battery for one minute, its resistance springs up to 12,000 ohms in the dark (still gold anode), and 5,000 in light; but gradually falls off again till it shows only 22 per cent change from dark to light. On substituting its old companion, the Leclanché battery, it immediately becomes tractable, and ends up with its original sensitiveness.

Brass cell No. 6, which has given 85 and 88 per cent with Leclanché battery, appeared to be almost worthless with the bichromate cells, showing but little sensitiveness to light,—in one measurement, none at all; and in another, its resistance was actually less in dark than in light,—the figures being 540 and 750 ohms, respectively. But on putting it with the Leclanché, its action changed, it became fairly sensitive to light, and behaved more like its old self.

Brass cell No. 12 also failed with the bichromate battery

and became entirely insensitive to light, showing no change whatever between light and dark.

Brass cell No. 5, when connected with the bichromate battery, refused from the first to show any sensitiveness at all. Its resistance varied continually, from high to low, and up again,—most of the time changing too rapidly to admit of getting any measurement. Changing the battery power from 12 cells to 24, 48, and 96 cells made no difference,—it still refused to respond to light, although reversing the current varied the resistance considerably. When one cell of the Leclanché battery was substituted, it started at 10,100 ohms in dark, and 5,700 ohms in light,—nearly 44 per cent decrease in light.

Doubtless other cells would have shown the same action, had there been time to test them, but these are sufficient to excite one's surprise. As before stated, the bichromate batteries had about the same surface in the liquid as the Leclanché. But even supposing that the current of the former had much greater quantity, intensity, or both, we might expect a change of resistance, *but how could it affect the sensitiveness of selenium to light?* If one kind of battery current destroys its sensitiveness, may we not suppose that another kind of battery might increase its sensitiveness? Although the Leclanché has operated well, some other may operate still better, and by its special fitness for use on selenium cells may intensify their actions, and so bring to light other properties yet unthought of. If so, where is the limit to this method of exalting the properties of selenium?

Is not here a promising field for experiment, in testing the various forms of battery already known, or even devising some new form especially adapted to the needs and peculiarities of selenium cells?

4th. The effect of intermittent currents, and of rapidly alternating currents, is usually very slight and may be disregarded in practical work. But occasionally they produce very surprising changes. Sometimes they reduce the resistance of the selenium cell from many thousands of ohms to almost nothing, and at others they raise it from next to nothing up among the thousands. I have not been able to ascertain any connection between conditions and results, but the effects are certainly remarkable. They are not due to my mode of arranging the parts of the cells, for the same thing occurs with other forms, as for example:

Experiment 1. The large "strip" cell measured, in the dark, 1,600 ohms. "Tried intermittent current. Needle erratic,—finally settles at 2,600 ohms." This experiment was with 22 cells of Leclanché. On trying the same experiment on an-

other day, no effect was produced, although the conditions were the same, so far as I could detect.

Experiment 2. Double cell No. 1, measured 50,000 ohms. Put on an automatic reversing apparatus (arranged to both break circuit and reverse the current about 300 times per minute), with 22 cells of Leclanché, for three minutes. The cell then measured, under the same conditions as before, only 30,000 ohms. A repetition of this treatment produced no further effect. The change, produced as described, was permanent.

The action of both intermittent and alternating currents upon selenium are worthy of careful study, for under certain conditions they are capable of effecting great changes in its resistance, which might be utilized for practical purposes if those conditions were understood.

5th. Very moderate changes of temperature (say 10° to 50° Fahr.), can sometimes change the resistance of a selenium cell hundreds or even thousands of ohms in a few seconds, and I think that this phenomenon has not been observed by others.

Experiment 1. Brass cell No. 6 measured, with gold anode, 23 cells Leclanché, in dark, 3,500 ohms. It was laid with its back upon an iron block warmed to about 100° Fahr., when its resistance fell almost instantly to 2,900 ohms, being a fall of 600 ohms.

Experiment 2. The same cell, in the same conditions at another time, measured 3,600 ohms. On putting the hot block under it, it fell to 2,400 ohms; in 30 seconds more it fell to 2,000 ohms; in another 30 seconds, to 1,850 ohms; in two minutes more to 1,600 ohms. By this time the block was but slightly warm.

Experiment 3. A cold block (i. e., not heated), was then put under the cell, when it rose at once to 1,920 ohms; in 30 seconds more, to 2,000 ohms; and continued to rise rapidly to 3,010 ohms. On repeating experiments 2 and 3, similar results were again obtained.

It will be observed that these effects were obtained by very small changes of temperature, and the phenomenon is distinct from the ordinary changes in electrical conductivity observed at different temperatures of the conductors, as well as from those produced by very high temperatures. The fact that an increase of temperature, so slight that the heated block barely feels warm to the hand, can change the resistance of a selenium cell many hundreds and even thousands of ohms, almost instantly, and that the withdrawal of so little heat can produce a change in the opposite direction, almost as great and as rapidly, is one of some importance, and has not been published before, so far as I am aware.

This action is more prominent in brass cell No. 6, than in any of the others. The same experiment tried with iron cell No. 1 produced no perceptible change in the resistance.

Experiment 4. Double cell No. 1, measuring 33,000 ohms, was laid on warm blocks, and fell instantly 3,000 ohms, then sank rapidly to 22,000 ohms. The same experiment, with double cell No. 2, the mate to No. 1, produced hardly any effect. When the "strip" cell was tried in the same way, it fell slowly, from 1,023 ohms to 955 ohms, in about five minutes. This action therefore appears to be exhibited much more strikingly by cells of my form than by those heretofore made. But why it occurs with some cells and not with others, has not been ascertained. The sensitiveness to light is greater when the cell is cold.

New form of Selenium.—Since the foregoing paragraphs were written, I have been trying some experiments long contemplated, and have succeeded in producing *colorless, transparent selenium.*

It is well known that vitreous selenium when very thin becomes translucent and has a beautiful ruby red color. The new form of selenium just discovered by me has no color, but looks like a thin coating of glass, through which the yellow brass base is clearly seen,—even the fine scratches and marks left in the brass from the polishing being as distinct as if the metal were bare. The mode of obtaining it is such as to exclude everything but selenium. The conditions of its production are these: The exposure of the selenium to a prolonged heating, followed by gradual cooling, under pressure. The plates so made have portions which are transparent, situated apparently where the temperature was highest. The remaining portions of the plates are black and red, interspersed with gray. Thus upon one plate may be seen selenium in four different states or colors. As yet, I have been able to make only a partial examination of one of these plates. A small portion of the transparent selenium having, perhaps, one-half square inch of surface, had a resistance of only three ohms. It was found to be affected by light very little, if at all.

As circumstances compel me, much against my will, to devote most of my time to a widely different branch of science, I do not wish to stand in the way of those who would work out these subjects more rapidly, and therefore offer my results for their consideration, and leave further researches to be carried out by any desiring to do so who may have more time and better facilities than myself for theoretical investigations.

TABLE A.

SELENIUM CELL, TESTED BY DR. WERNER SIEMENS.

Selenium in	Relative Conductivities.		Resistance in Ohms.
	Deflection.	Ratio.	
1. Dark	32·	1·	10,070,000
2. Diffused daylight	110·	3·4	2,930,000
3. Lamplight	180·	5·6	1,790,000
4. Sunlight	470·	14·8	680,000

TABLE B.

SELENIUM CELL, TESTED BY THE AUTHOR.

Resistance in Ohms.

Brass Cell, No. 16.	Test No. 1.	Test No. 2.	Test No. 3.	Test No. 4.	Test No. 5.	Test No. 6.	Test No. 7.
Dark	210·	210·	170·	110·	210·	219·	395·
Diffused daylight	49·	14·	53·	13·	110·	90·	72·
Per cent of change	76·6	93·3	68·8	88·1	47·6	58·9	81·7

Note.—A paper on "The Action of Light on Selenium," by Professor W. G. Adams, F.R.S., and Mr. R. E. Day, in Proc. Roy. Soc., vol. xxv, p. 113, contains the following statements:

1st. That on reversing the direction of the current through selenium the "resistance was always found to be different from that previously obtained." As I have shown, the resistance is not always different.

2d. "The first current through the selenium, if a strong one, causes a permanent 'set' of the molecules, in consequence of which the passage of the current during the remainder of the experiments is more resisted in that direction than it is when passing in the opposite direction." As already stated, this "set" is sometimes in the direction above laid down, sometimes in the opposite direction, sometimes there is no "set" at all, and in two cases the "set" *changed* and was reversed during the measurements of the cells.

3d. "That with the same piece of selenium at the same temperature, the resistance diminished as the battery power increased." This I have found by experiments with more than one hundred cells to be correct in some cases, while the opposite occurs in other cases, and in still other instances the increase or decrease of resistance stops at a certain battery power, and is then reversed.

It will be seen that their experiments and results were entirely different from mine, except on the three foregoing points. As to them, so far as the above quotations agree with my results, those investigators are entitled to the credit of first discovery.

New York City, Aug. 28, 1883.