

## ON SOME PECULIARITIES OF ELECTRICAL CONDUCTIVITY EXHIBITED BY POWDERS AND A FEW SOLID SUBSTANCES.

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THE unilateral conductivity of the mercury arc and the electrolytic cell, the lack of proportionality between E.M.F. and current in the arc and in contact rectifiers, and the change of resistance with time in the case of some heated substances are well-known anomalies of electrical conductivity. The purpose of this paper is to describe some new cases of this sort, which may, perhaps, lead to a new point of attack of the questions of asymmetrical conduction in contact rectifiers, and also of the problem of the coherer.

## OUTLINE OF THE WORK.

The work herein described grew from a study of the conductivity of loose powders, a subject on which, so far as the writer has been able to learn, practically no work has been done (except in the case of the coherer). In investigations where the specific resistance of salts has been measured, the substances, although existing after purification as powders, have in all cases been submitted to pressures in the neighborhood of 10,000 atmospheres before any measurements of the resistance have been taken.

In the work described in this paper, the writer investigated chiefly three phenomena of conduction through loose powders and certain solid substances: (1) Change of conductivity with time. (2) The development of asymmetry of conduction, that is, difference of conductivity in the direction of and opposite to the current. (3) Deviation from Ohm's law.

## APPARATUS.

The resistance of the powders examined was very high—*e. g.*, the mean of two values of the specific resistance for powdered cal-

cium sulphide was  $1.72 \times 10^7$  ohms. Thus the conductivity could only be measured by using a thin, wide layer of the powder, a high E.M.F., and a sensitive galvanometer. The apparatus is shown in

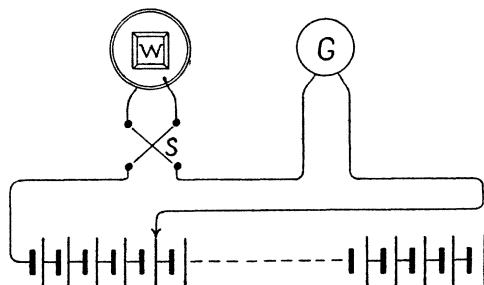


Fig. 1.

Fig. 1. The powder was sprinkled over a flat copper disk 6 inches in diameter to a depth of about a millimeter. Then a similar disk on which was a lead weight  $W$  was placed on this layer. This resistance, or bridge (as a conductor of high resistance will be called, for lack of a better term), was placed in series with a sensitive Broca galvanometer  $G$ . An E.M.F. was applied by a battery of forty small storage cells, so that the E.M.F. could be varied by steps of closely two volts from 0 to 80 volts. A reversing switch  $S$  was provided. Throughout the work the galvanometer sensibility was  $7.156 \times 10^{-8}$  amperes per mm. of the scale.

The substances studied were the sulphides of calcium, barium, zinc, and mercury, sulphate of calcium and of mercury, calcium fluoride, barium carbonate, magnesium oxide, mercuric oxide, mercurous oxide, litharge, zinc-dust, mercuric iodide, solid silver iodide, borax, zinc perborate, selenium, and molybdenite.

Of the solid substances used in the experiments, the silver iodide bridge was made by fusing precipitated silver iodide on a glass plate on which had previously been bound two platinum wires, .5 cm. apart, as electrodes. The silver iodide was heated highly so as to reduce some of the silver, to aid in the conduction, and in some cases a trace of silver nitrate was added. This bridge, when cold, had a high resistance, but not so high as to make readable deflections impossible.

Barium sulphide, in the form of hard lumps, was ground down on an emery wheel and finally filed into the form of thin disks.

The mineral molybdenite — the other solid substance examined — was split into thin plates. The other substances call for no special mention.

#### CHANGE OF CONDUCTIVITY WITH TIME.

It has been observed<sup>1</sup> that when certain solid sulphides, lead sulphide and silver sulphide, are heated by the passage of a current through them, the conductivity increases greatly. On removing the heating current, it is found that the conductivity falls to its original value, then falls somewhat below it, thence slowly increasing to the original value, in about 40 minutes. Other than this, the conductivity of substances — excepting in the electrolytic state — does not change with time.

In the case of the powders and solids here considered, however, the conductivity varied with the length of time the current was applied, at ordinary temperature.

In most cases, when an E.M.F. was applied, the conductivity fell very rapidly at first, then more and more slowly, approaching a limiting value, many times less than the original conductivity. If, after this exposure had continued for some time the circuit was broken, the conductivity slowly regained its original value, the increase being most rapid at first. When the exposure was long enough to make the conductivity constant, the state of the substance seemed fairly steady, that is to say, if the circuit were opened for a short time and then closed, the conductivity soon regained the steady value before the interruption. It was found, in this way, that a momentary breaking or even reversing of the current, did not change appreciably the conductivity of this steady state. Thus it may be assumed that in studying the rise of conductivity after exposure to the steady E.M.F., momentary application of the E.M.F. to get a deflection did not change the conductivity of the substance appreciably.

This change of conductivity with time differed both as regards magnitude and direction with various substances. Of the powders used, calcium sulphide gave the greatest change in magnitude. On one occasion, after an exposure to the E.M.F. of three days, the conductivity rose 60 fold in 21 hours. The initial changes produced in calcium sulphide by the E.M.F. were too rapid to be

<sup>1</sup> Streintz, *Phys. Zeit.*, 4, p. 106, 1903.

recorded. A curve is, however, given (Fig. 2, *I*) showing the effect of application of the E.M.F. to a specimen of calcium sulphide, 40 minutes after a previous, long, application. The first part of the curve shows the effect of the steady application — the second part, the effect after the E.M.F. was removed, it being applied then only long enough to take readings.

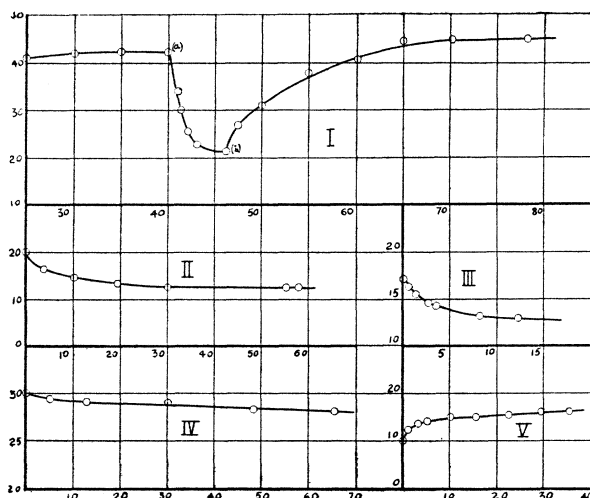


Fig. 2. Time-conductivity change for *I*, calcium sulphide, current applied during (*a-b*); *II*, zinc sulphide; *III*, magnesium oxide; *IV*, strontium sulphide; *V*, solid barium sulphide. Ordinates, deflections, abscissæ, time in minutes.

The substances which exhibited a decrease of conductivity on continued passage of a current were — arranged in the order of magnitude of the effect — calcium sulphide, barium sulphate, borax, zinc sulphide (Fig. 2, *II*), magnesium oxide (Fig. 2, *III*), mercurous sulphide, mercuric sulphide, zinc dust, calcium sulphate, solid silver iodide, strontium sulphide (Fig. 2, *IV*) and litharge.

Those exhibiting an increase were — solid molybdenite, barium carbonate, powdered barium sulphide, solid barium sulphide (Fig. 2, *V*), and red iodide of mercury.

Barium fluoride, zinc perborate, and selenium, all powdered, showed neither increase nor decrease to any appreciable extent.

#### EFFECT OF a VACUUM.

All the powders that were examined, except selenium, and even the solids, silver iodide and barium sulphide, showed a marked effect

when the vessel in which they were contained was exhausted by an air pump. The effect in nearly all cases was the same — a great decrease in conductivity, the change persisting until air had been readmitted, following which there was a gradual rise. With magnesium oxide, the conductivity was reduced to one ninth the initial value by the vacuum, and with other substances the change was comparable with this. The behavior of calcium sulphide is illustrated by Fig. 3, *I*. For all other substances, except solid barium sulphide, and molybdenite the curves are similar. With barium

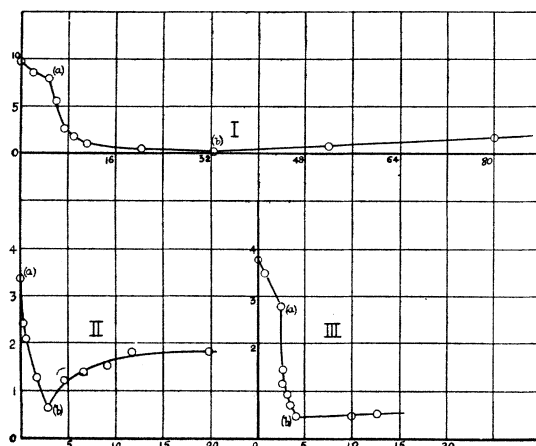


Fig. 3. Effect of a Vacuum on the Conductivity of: *I*, Calcium sulphide; *II*, solid barium sulphide; *III*, powdered barium sulphide. (*a*) Vacuum produced, (*b*) air admitted. Ordinates, deflections, abscissæ, time in minutes.

sulphide the rise on admitting air was somewhat abrupt (Fig. 3, *II*). When the barium sulphide was powdered, the curve obtained resembled that for calcium sulphide (Fig. 3, *III*) as did also that for the *solid* silver iodide. Solid molybdenite appeared to give a rather sudden fall in conductivity of about 15 per cent. on producing the vacuum, and a corresponding rise on admitting air.

The effect seemed to be more or less independent of the current. With CaS, when the E.M.F. was applied for a short time, at intervals of two minutes *after* exhaustion, the deflections corresponding to these applications kept growing smaller. After admitting air, they kept increasing. A vacuum now caused them to decrease and a readmission of air caused them to increase.

An E.M.F. was applied steadily to CaS until the deflection had reached a fairly steady value. The E.M.F. was then removed, and a vacuum produced. On reapplication of the E.M.F. the deflection was found to be only 20 per cent. of that just before exhaustion. When the conductivity was at its lowest, under the influence of a vacuum, jarring the bridge caused a rather feeble rise, but after the air had been readmitted and the conductivity had risen, jarring caused a considerable rise.

Later experiments have indicated that the proportionate drop in deflection, after a one-minute application of the vacuum, is the same whether the E.M.F. has been applied for a very short time, immediately before producing the vacuum, or for five minutes.

#### FURTHER OBSERVATIONS.

The powders differed markedly as regards fineness. The calcium sulphide, barium fluoride, magnesium oxide, and the carbonates and sulphates were all very fine. The zinc sulphide was somewhat coarse, while the selenium was the coarsest of all. The other powders were nearly, if not quite, as fine as those first mentioned. The resistances of the powders differed widely, but the copper disks could be used for all powders except zinc dust, which had to be used in a glass tube resembling a coherer.

No polarization, or back E.M.F., could be observed at any time. If the bridge — or system containing the powder — were short circuited across the galvanometer, no swing followed. Only when the resistance of the powder was so extremely high that readings could not well be taken could a deflection be observed — the bridge then acting as a condenser.

In the experiments described, copper electrodes were used, but no apparent change was produced when the electrodes were tin, zinc or platinum.

The powdered sulphides gradually produced a thin, bluish film of sulphide on the copper electrodes. This did not influence the results, as a bridge, allowed to stand for three days after having been freshly prepared, showed the same phenomena as a bridge tried immediately after being made.

It was found that after the conductivity of the calcium sulphide had fallen to a fairly steady value, under the influence of an E.M.F.,

the disks with the powder between them could be disturbed in certain ways without changing much the value of the conductivity at that time. When the current was removed for a moment and was then applied again, the conductivity was found to have risen, but it soon fell back to the steady value. If the upper copper disk were now lifted off very carefully, and then replaced, the conductivity was likewise found to have risen, but it soon fell back to the steady value. If, however, the powder itself were stirred or jarred, the conductivity, after the disturbance, was found to have risen much higher — the bridge behaving as if freshly prepared.

The action of a powder, as regards the time-conductivity change, is not always the same. In many trials at different times, calcium sulphide and borax showed a decrease of conductivity with time. Once, however, for each powder, there was an exception, for no apparent reason. The rise with time in the case of calcium sulphide was almost linear, the curve being slightly convex toward the time-axis, while the curve for the borax resembled the hysteresis curve for iron, being S-shaped. These cases could not be repeated.

A peculiar time-conductivity effect was noticed with barium sulphide, which might be called a spontaneous rise of conductivity. It was found that when the barium sulphide was freshly powdered, the conductivity rose to three times its initial value in 3.5 minutes, the E.M.F. being applied only long enough to take readings. To investigate this further, a sample of freshly powdered barium sulphide was divided into two parts; one was placed in a vacuum desiccator for twenty hours, and the other exposed to the air of the room for the same time. The conductivity of the former part was found to rise slowly after removal from the desiccator, increasing by one third in twenty minutes, while that of the latter decreased to about one half in two minutes — in each case the E.M.F. being applied only long enough to take readings. When the E.M.F. was applied steadily, the conductivity fell in both cases. To find whether or not the applications of the E.M.F. for a short time were important, a third experiment was performed. Two bridges, as nearly equal as possible, were made from freshly powdered barium sulphide. The conductivity of one, I., was observed immediately

after setting up — the other, II., not until five minutes later. After this the conductivity of both was observed at the same time for five-minute intervals for an hour. Bridge I. gave a somewhat greater conductivity at first, but both gave decreasing values (Fig. 4). After the experiment represented by Fig. 4 was performed, the

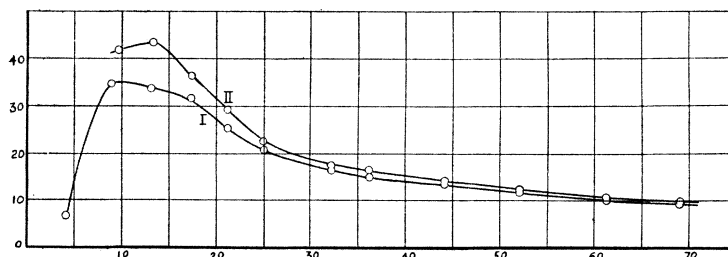


Fig. 4. Spontaneous Rise in Conductivity, freshly powdered Barium Sulphide. *I*, Bridge no. 1, ordinates, deflections; *II*, Bridge no. 2, abscissæ, time in minutes.

powder was stirred, and the experiment was repeated. This time, the conductivity also rose, but to a much less extent. A later experiment has indicated that the conductivity may increase and remain large if the E.M.F. is not applied often.

A nickel-silver coherer of the ordinary type was examined under various conditions to detect, if possible, a time-conductivity effect, but the results were not consistent. At times, however, the application of an E.M.F. caused a sudden decrease of conductivity, while its removal caused a gradual rise.

#### ASYMMETRIC CONDUCTION.

Certain cases in which conductivity in the direction in which the current is flowing is different from that in the reverse direction are common. Examples of these are the battery, in which a back E.M.F. exists, and the mercury vapor lamp, where a stream of charged particles tends to carry the current in one direction. There are also cases of contact between substances — usually point contact — where the same peculiarity of conductivity exists. It has been shown<sup>1</sup> that, while contacts of silicon and steel, carbon and steel, and aluminium and tellurium act as alternating-current rectifiers, they also exhibit unilateral conductivity with direct cur-

<sup>1</sup> Austin, Bull. Bur. Standards, 5, 1, p. 133, 1908.



rent. With the aluminium-tellurium contact, the effect with direct current may be observed even if a no. 20 aluminium wire is melted into a block of tellurium.

It is not necessary, however, that the contact should be that of different substances. It has been found<sup>1</sup> that if a coherer formed by two copper wires touching each other is made to cohere in the ordinary manner, by a spark some distance away, the wires, if separated and held apart a few moments, will not re-cohere when placed together again, but will do so if the current be reversed. The wires may be again separated and the action repeated several times.

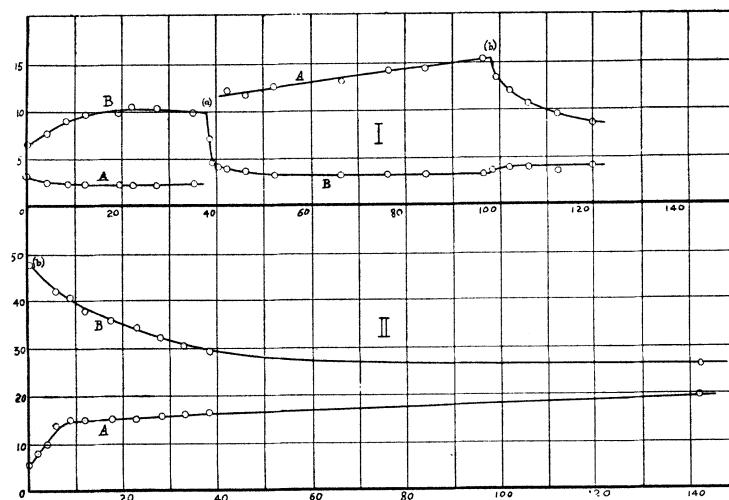


Fig. 5. *I*, Asymmetric Behavior of Calcium Sulphide; *II*, Recovery of Calcium Sulphide after 1 hr. 22 min. exposure to the E.M.F. (*a*) Current reversed, (*b*) circuit opened. Ordinates, deflections, abscissæ, time in minutes.

The effects to be described resemble those just considered. It will be convenient to call *A* the conductivity in the direction of the initial current, and *B* the conductivity in the opposite direction.

The relation between *A* and *B* for calcium sulphide is shown by Fig. 5. The current was kept constantly in the direction *A*, and brief reversals for *B* were made at intervals of two minutes, only long enough to take a reading. The current was then reversed, and it will be noticed that here *A* rose steadily while *B* fell. This illustrates the steady increase of conductivity in the direction opposite to that in which the current is flowing, characteristic of calcium

<sup>1</sup> Shaw and Garret, *Phil. Mag.*, 8, p. 164.

sulphide. On opening the circuit, and taking readings for the conductivity at intervals of two minutes — applying the current for as short a time as possible — *A* fell, while *B* kept rather constant. It is to be noted that the deflection for *A* reached a steady value quickly. For *B*, however, the initial throws grew larger and larger, falling rather rapidly to the same scale division each time. The resistance, then, *increased* in one direction, on opening the circuit. The specimen of powdered calcium sulphide used in this experiment had been previously subjected to reversals.

Two fresh bridges of calcium sulphide were then prepared. One was exposed to the E.M.F. for 18 minutes. When the circuit was opened, *A* fell slightly, then rose, while *B* rose, as it had been doing before the E.M.F. was removed. The other bridge was

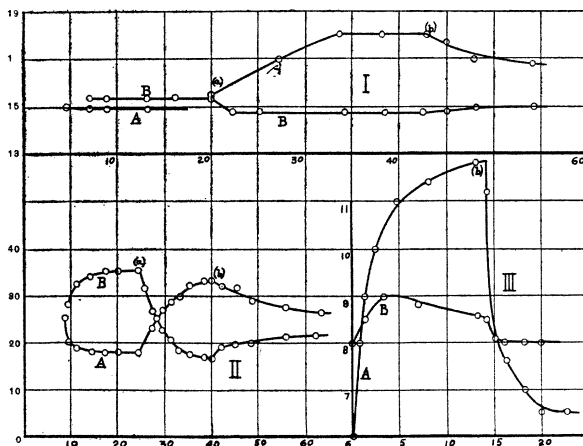


Fig. 6. Asymmetric conduction in : *I*, Selenium ; *II*, solid silver iodide ; *III*, molybdenite. (*a*) Current reversed, (*b*) circuit opened. Ordinates, deflections, abscissæ, time in minutes.

exposed to the E.M.F. for 1 hour 22 minutes. Here the increase in resistance on opening the circuit was clearly marked (Fig. 5, *II*).

The behavior of coarsely powdered selenium was peculiar. At first the difference between *A* and *B* was not marked (Fig. 6, *I*), but on reversal of the current the conductivity in the direction of the current then flowing fell slightly, while that in the opposite direction rose considerably. The effect on opening the circuit was similar to that of calcium sulphide after a long exposure to the

E.M.F. The conductivities, on reversing, appeared to reach a steady state after a short time. For example, in one case the initial deflections were  $A$ , 15;  $B$ , 16.8; an E.M.F. was applied, for 88 hours, after which they were,  $A$ , 14.5;  $B$ , 15, rising quickly to 22. After several reversals a steady state was obtained with  $A$ , 15;  $B$ , 22.

The bridge of solid silver-iodide described above, showed the asymmetry markedly. The current fell in the initial direction and rose in the opposite direction. This was true on reversal, Fig. 6, *II*. It should be noticed that with this substance the curves for  $A$  and  $B$  are of the same shape, one of them being inverted. With this substance, when a vacuum was produced,  $A$  dropped to one fourth its value, while  $B$  dropped to two fifths its value before the production of the vacuum.

The mineral molybdenite behaved differently from the other substances examined, in that  $A$  increased with the time, while  $B$  fell. After applying the E.M.F., the conductivities soon reached a steady state. The phenomenon was here complicated by the fact that a given state in the molybdenite tended to persist. In other words, with a perfectly fresh specimen, the E.M.F. produced a state which persisted for a considerable time — the conductivity for this initial direction being permanently above that in the reverse direction. The effects of subsequent reversals were superposed upon this permanent effect. The molybdenite showed the effect clearly after standing for a day. It could be removed from between the copper plates or electrodes, turned over and replaced, and would show the same effect if the conductivity were measured with a current in the *same direction* through the specimen as before. The state could be obliterated, however, if the specimen were split into laminæ, and some of these were reversed. This state was, curiously, influenced by sparks from an induction coil, several feet away from the apparatus. After a spark had passed, the state was often reversed, and the conductivity, in general, was higher. Such sparks had no apparent influence on the other substances examined. Fig. 6, *III*, shows the changes in conductivity of a specimen of molybdenite, with a permanent state, after standing over night. It will be noticed that  $B$  tended to be permanently above  $A$ . In this experiment  $A$  and

*B* were in the same direction for a short time after applying the E.M.F.

Asymmetry was found with a coherer of the ordinary form, made of nickel-silver filings. A state of asymmetry would appear more or less suddenly, remain rather constant, and persist even if reversals were made rapidly. The tendency seemed to be for *A* to remain steady and for *B* to rise, and *B* could stay permanently twice *A*.

When reversals were made, in studying asymmetry, a certain sluggish action was noticed with selenium which was not shown with the other substances. When the current was flowing in the direction *A*, in selenium, and a steady deflection had been reached, for both *A* and *B*, a reversal gave immediately the larger deflection for *B*, but a reversal back to the original direction did not give the original deflection at once, but the deflection fell rather slowly from the higher.

#### DEVIATION FROM OHM'S LAW.

The substances that were studied did not show a proportionality of current to E.M.F. In other words, the conductivity depended upon the applied E.M.F.

As has been said, after the E.M.F. had been applied long enough to bring the conductivity to a constant value, it could be removed for a moment, and when reapplied the same conductivity would be shown. It was found that, if the E.M.F. were removed, and various other E.M.F.'s applied in rather rapid succession, readings could be taken of the deflections corresponding to these other E.M.F.'s, which would be perfectly definite and not depend upon the order in which they were applied, and that after this had been done, the original E.M.F. produced closely the original deflection. Hence, at any particular time, agreement with Ohm's law could be tested.

A calibration curve was first made for the galvanometer by applying equal steps of voltage from across a slide-wire in series with a high resistance. The curve in which these increments were plotted against the corresponding deflections was a straight line.

All the powders and the three solids examined showed deviation from Ohm's law, except powered zinc perborate. Arranged in the order of magnitude of the effect; *i. e.*, the magnitude of the curva-

ture, they were, molybdenite (Fig. 7, *I*), calcium sulphide, solid barium sulphide (Fig. 7, *IV*), powdered barium sulphide, mercuric

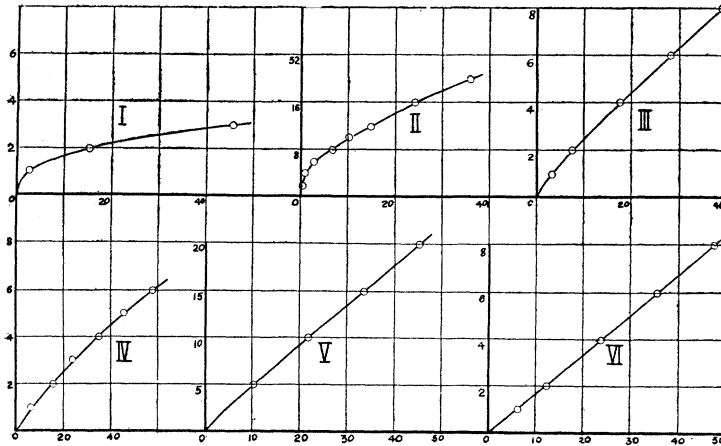


Fig. 7. Deviation from Ohm's Law of: *I*, Solid molybdenite; *II*, solid barium sulphide; *III*, magnesium oxide; *IV*, strontium sulphide; *V*, solid silver iodide; *VI*, zinc perborate. Ordinates, potential by storage cells, abscissæ, deflection.

oxide, zinc dust, magnesium oxide (Fig. 7, *III*), borax, strontium sulphide (Fig. 7, *IV*), mercuric iodide, barium carbonate, barium sulphate, barium fluoride, zinc sulphide, solid silver iodide (Fig. 7, *V*), calcium sulphate, litharge, mercurous oxide, and zinc perborate (Fig. 7, *VI*), which last gave no sensible deviation whatever. From the curves it is seen that those substances which deviate but slightly do so most strongly at low voltages. In these curves, the ordinates represent the number of storage cells used in obtaining the E.M.F.

The deviation from Ohm's law was present under all conditions except when great pressure was applied. A heavy press used for making pellets for a bomb calorimeter was used to furnish the pressure on a specimen of powdered calcium sulphide. As the pressure was increased, the curves approached a straight line. Figs. 8, *I*, *II* and *III* show the relation between current and E.M.F. before applying pressure, with considerable pressure, and with the greatest possible pressure, respectively. It will be noticed that Fig. 8, *II*, resembles the curve for selenium.

Even in a vacuum, the deviation from Ohm's law was present.

The marked change in conductivity necessarily caused a change in the curvature, as is evident from Figs. 9, *I*, *II*, *III*.

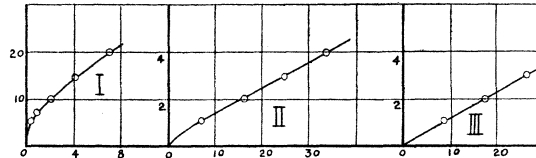


Fig. 8. Effect of Pressure on the Deviation from Ohm's Law in Calcium Sulphide: *I*, Before applying pressure; *II*, with considerable pressure; *III*, with great pressure. Ordinates, potential, by storage cells, abscissæ, deflection.

The deviation did not disappear with current densities many times greater than those ordinarily used in the experiments. When the current density, as indicated by the shunted galvanometer, was increased to 300 times the usual value with calcium sulphide, requiring the application of 40 volts, Ohm's law was not obeyed. When, however, 60 or 80 volts were applied, the current became much larger, and very irregular.

No difference in the effect could be detected after the calcium sulphide had been placed on a glass plate in a closed vessel over water for a day, or in a vacuum desiccator over sulphuric acid.

An electric discharge had a marked defect on the conductivity of zinc-dust, but did not change the deviation from Ohm's law to any

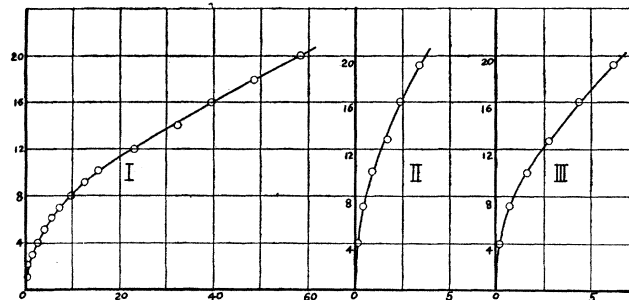


Fig. 9. Effect of a Vacuum on the Deviation from Ohm's Law in Calcium Sulphide: *I*, Before the vacuum; *II*, during the vacuum; *III*, immediately after the vacuum. Ordinates, potential, by storage cells, abscissæ, deflection.

appreciable extent. As the conductivity of zinc-dust was better than that of the other powders used, it was possible to make a bridge

of it in the form of a tube coherer. The tube of the coherer was placed one inch from the spark gap of a small induction coil, parallel to the axis of the gap. It was found that sparks caused the conductivity of the zinc dust to increase about 100 fold, but, when steady readings were possible, the deviation was still present. After the sparking, the conductivity of the zinc-dust coherer fell, whether the current were on or off.

A peculiarity of the deviation is that, with the same substance, the upper part of the  $E$ - $I$  curve is more or less straight. Here, again, there seems to be a general tendency, which is followed except in a very few cases.

The above phenomena, in general, may reasonably be considered as contact phenomena; *i. e.*, changes taking place at the junctures between particles. It is evidently so for powders, and is more or less so in the case of solid silver iodide, barium sulphide, and molybdenite, if it be assumed that, in the first two bodies, there is point contact between the interlocking crystals, and, in the last, line contact between thin laminæ.

This being so, there should be some resemblance between the behavior of powders, and of the coherer. Such a resemblance can be seen by a consideration of what has been already found concerning coherer phenomena.

#### THE CONDUCTIVITY OF THE COHERER.

##### (a) *Particle-coherers.*

It has been found<sup>1</sup> that a film of some sort is necessary between the coherer particles. For example, silver filings cannot be used as a coherer, but can be, after exposure to hydrogen sulphide. If exposed too long, however, the efficiency falls off, the film becoming too thick.

Sparks usually pass between the particles. Minute sparks have been observed microscopically even with particles surrounded by Canada balsam.<sup>2</sup> They have also been observed, between steel, across a gap of 0.006 mm., before a galvanometer indicated a cur-

<sup>1</sup> A. Blondel, *Écl. Élect.*, 16, p. 316, 1898.

<sup>2</sup> L. Arons, *Ann. Phys. Chem.*, 63, 3, p. 567, 1898.

rent. Small particles were observed to fly across before a bridge formed.<sup>1</sup>

Fusions take place at the contacts. This has been shown by producing coherence in a coherer of iron filings and subsequently removing the loose filings with a magnet, leaving the chains of particles;<sup>2</sup> also, by producing coherence in a tube of brass filings, and observing that the resistance lengthwise of the tube was very much lower than that transversely.<sup>3</sup>

As the pressure of particle on particle is increased, up to the pressure at which the particles come into actual metallic contact with each other, the coherer becomes more and more sensitive.<sup>4</sup>

Lowering the temperature of the coherer produces no result; raising the temperature produces decoherence.

The particles of a coherer may produce effects by being in motion. Brass turnings between two highly charged plates, in oil, may execute an "electric dance," carrying charges to and fro until the turnings finally become welded together as chains.<sup>5</sup> Besides this action, charges on adjacent particles must exert forces tending to draw the particles together. This has been given<sup>6</sup> as an explanation of the deviation of the coherer from Ohm's law. When a coherer is regularly tapped many times a second to produce decoherence, definite deflections of a galvanometer may be had when various E.M.F.'s are applied. The curve giving the relation between  $E$  and  $I$  is not, however, a straight line, but is concave toward the axis of  $I$ , becoming approximately linear with increase of  $E$ . There is apparently no critical voltage. Eccles explained this on the supposition that the particles are free to move, are not circular, and hence are acted upon by a couple, which tends to pull the long axis in line with the current. The  $E$ - $I$  curve showed initial curvature in all cases, the curvature persisting for the higher values of  $E$  with non-sensitive coherers. (It is to be noted here that in the work described in the present paper all the powders and solids

<sup>1</sup> J. Hården, *Electrotech. Zeit.*, 21, p. 272, 1900.

<sup>2</sup> T. Sundorph, *Wied. Ann.* 68, 3, p. 594, 1899.

<sup>3</sup> F. Campanille and G. di Ciommo, *Elect. Rev.*, IV., V., 36, p. 353, 1900.

<sup>4</sup> P. Jegou, *Écl. Élect.*, 51, p. 82, 1907.

<sup>5</sup> R. Malagoli, *N. Cimento*, 10, p. 279, 1899.

<sup>6</sup> Eccles, *Electrician*, 47, p. 682, p. 715, 1901.



examined except molybdenite were insensitive to Hertz waves.) The straight part of the curve, then, is reached when most of the particles have turned with their long axes in the direction of the current. This theory, however, seems somewhat disproved by the fact that the same curves have been obtained with nickel filings in kerosene<sup>1</sup> where the resistance to turning ought to be much greater.

(b) *Ball-coherers.*

Where the contact is between particles of considerable size, fusion takes place on coherence, as has been shown<sup>2</sup> by the fact that, when two copper wires cohere, it requires a small but measurable pull to separate them.

The conductivity of the ball-coherer has been carefully studied,<sup>3</sup> by means of a coherer, one of the balls of which was held by a spring and could be given a fine adjustment with a screw. Sparking and the attending complications was avoided. When both contacts were heated, the resistance of the coherer decreased, regaining the initial value on cooling. When one contact only was heated, the resistance was different in the two directions—the potential difference of the coherer being lower when the electricity flowed from the hotter to the colder side. For a considerable range, the resistance did not depend on the pressure between the balls.

The deviation from Ohm's law was peculiar. As the E.M.F. was slowly increased, the current increased, at first slowly, and then more and more rapidly, the E.M.F. approaching a constant value, the critical voltage, which was characteristic of each metal. Guthe and Trowbridge explained this by considering that as the E.M.F. becomes greater, the tension across the film at the contact increases, and ions break through and conduct. The more filled up this area of film is, the less readily the ions go over, thus creating a tendency for the area of contact to become greater and greater and the potential difference to become less and less with increasing current until the critical voltage is reached. As the potential does not vary through a considerable range of current, we cannot have to do with a time rate of heaping up of ions. It is a curious fact that the

<sup>1</sup> Huth, *Phys. Zeit.*, 4, p. 594, 1903.

<sup>2</sup> Shaw and Garret, *loc. cit.*, p. 413.

<sup>3</sup> Guthe and Trowbridge, *PHYS. REV.*, 11, p. 22; 12, p. 245.

product of the critical voltage and the atomic weight is approximately a constant.

Guthe and Trowbridge explained negative action, or the increase of resistance of a coherer under increasing excitation, by considering that, when this action takes place, a small particle is lodged between two larger ones, from which position it is displaced — thus increasing the resistance — when the potential difference between the larger particles is increased.

This was found experimentally to be so. Such negative action takes place with powdered lead dioxide and some of the soft metals. With feeble waves there is coherence, but with powerful waves there is a relapse to the state of high resistance. A former explanation of this was that the feeble waves produce bridges which are broken down by the powerful waves.

Asymmetry has been shown by Shaw and Garret<sup>1</sup> to exist for a coherer of two copper wires. It was suggested by the authors, that, as the current density at the points of contact is enormous, an orientation of the particles forming the bridge takes place, "the particles being turned in such a way that they give maximum conduction."

#### ATTEMPT AT EXPLANATION OF THE CONDUCTIVITY OF POWDERS.

From a consideration of what has been found for coherers, an attempt may now be made to explain the conductivity of powders and of such solids as were examined. The fall, or rise, of conductivity with time had best be considered in detail along with asymmetry.

It seems improbable that the change of conductivity with time is due to a decohering action such as breaking of the chains of particles by heating produced at the junctions. Cooling a coherer produces no change, warming produces expansion and fracture of the junctions, hence decoherence. An experiment was performed to test this point with calcium sulphide. After a steady state of conductivity had been reached, the bridge was cooled to the temperature of ice. No change took place. After the ice was removed the conductivity rose during the warming. This suggests a like action in

<sup>1</sup> Shaw and Garret, *loc. cit.*, p. 413.

the two cases as a jarring produces a decrease of conductivity with the coherer, and an increase with calcium sulphide. Hence the time-conductivity effects would not seem to be due to a rearrangement of particles.

Irregularities might be expected with powders, as with the coherer, "negative action," for example. The occasionally capricious action as regards the time-conductivity effect in powders ought not, then, to appear remarkable.

Because the deviation from Ohm's law is always in the same direction, it must be due to some condition which holds for all powders. It may be explained most easily by supposing that, as the E.M.F. increases, particles that were loose now take part in the conduction either by movements, or by forming temporary chains of particles. The phenomenon may, however, not be so simple.

Since the study of a coherer shows that a surface film is necessary, it seems safe to assume that, with all substances which show change of conductivity with time or deviation from Ohm's law, a surface film is also necessary.

The spontaneous rise is difficult to understand unless it has to do with ionization on fresh surfaces that may be acted upon by the air, as suggested by the following consideration of asymmetry.

#### ASYMMETRY.

The phenomena connected with the asymmetric conduction of powders are very complex, and it is difficult to give any satisfactory explanation of them. Yet it is desirable to make some attempt at an explanation, however crude it may be. A theory which has been suggested to the writer by some of the views already advanced, has helped him to form some idea of what may take place in a powder that conducts asymmetrically. This theory may not be correct, and, even if it is found to be so, it will probably have to be modified greatly.

Asymmetric conduction for powders and the coherer may be explained by considering conduction to take place by means of ions in motion. Suppose in Fig. 10, which represents a contact between particles, greatly magnified, *A* to be the part of the film between the particles. This film is necessary in order to have coherence

phenomena, as there must be something which separates the particles, prevents fusion, and hence causes currents of great density at the points of contact. Suppose  $B$  and  $B'$  to be the respective parts of the two particles that are most highly heated,  $C$  and  $C'$  to be regions where the heating is less intense.

It will be necessary to make certain assumptions.

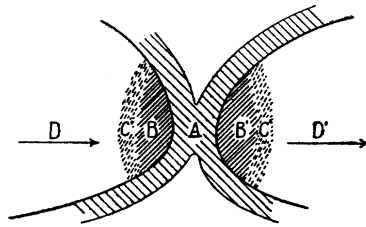


Fig. 10.

(a) Owing to the high temperatures at contacts between particles, due to great current density, there should be marked changes of the resistance to motion of electrons, or negative ions, which move across the contact. Hence assume the resistance to motion of the ions in the more heated regions,  $B$  and  $B'$ , to be greater or less than in  $C$  and  $C'$ , depending on the material of the particles.

(b) Also assume that the film  $A$ , though it may have considerable resistance, has small resistance, as a rule, compared with  $B$  and  $B'$ .

This will help to explain asymmetrical conduction in which the conductivity in the direction of the current decreases with time, while that in the opposite direction steadily increases. If the hotter parts  $B$ ,  $B'$  impede the negative ions more, then, if the current flows from  $D$  to  $D'$ , the ions produced in  $C$  will move slower as they approach  $B$ . Thus there will first be considerable movement of the ions until there is a kind of opposing assemblage in  $B$ . Ions will still pass through and beyond  $B$ , but at  $B'$  they will be neutralized by positive charges there, as  $B$  and  $B'$  are charged oppositely, and will not pass to any extent into  $B'$  and  $C'$ .

If now the current be reversed, the ions will move back *at a higher rate*, since they are all now moving in the direction of decreasing resistance, and this increased rate means a high initial current. Such a state of asymmetry is found with calcium sulphide and solid silver iodide.

On the other hand, if the regions  $B$ ,  $B'$ , and  $A$  offer less resistance to the motion than  $C$  and  $C'$ , which are cooler, then, when a current is sent from  $D$  to  $D'$ , ions from  $C$  will cross  $B$  to  $B'$ , where they will be neutralized as before. In this case they pass through a region in which they move constantly faster, *i. e.*, the current increases. A steady state is reached when the velocity at any point in the course remains the same.

If the current be now reversed, the condition will differ from that which initially held, in that the ions in  $B$  will all be moving in the direction of increasing resistance, and hence the current, depending on the rate of motion, will be small. It will increase, however, if time is given for the ions in  $C'$  to pass into  $B'$ . This is the case of molybdenite.

It is to be observed that this explanation of asymmetry takes care of the question of the change of conductivity with time.

Since, when the powder is in a vacuum the asymmetry is still preserved nearly unchanged, the vacuum must modify the film  $A$ , which is, perhaps, a kind of arc, possibly removing ions, and— to account for the slow rise of conductivity (see curve)— making subsequent passage of ions in  $A$  difficult, after this removal.

This theory of asymmetry receives support from certain experimental facts. It has been shown by Streintz<sup>1</sup> that solid silver sulphide when raised from  $-200^{\circ}$  to  $220^{\circ}$  falls in resistance from a very high value to 0.1 ohm. At the higher temperature a current of 1 or 2 amperes can be sent through a specimen for several hours without evidence of decomposition. There develops with time, however, an increasing resistance to the flow of the current, without any signs of electrolytic polarization being manifest. This may be due to a gathering of the ions in the poorly conducting substance, which opposes the current even though no polarization exists. The fact that the rate of decrease of resistance with temperature for mercury and lead sulphides is about one fourth that for silver sulphide suggests that the positive atom has something to do with the opposition to motion.

In the aluminium-tellurium rectifier already mentioned<sup>2</sup> it was

<sup>1</sup> Streintz, *loc. cit.*, p. 407.

<sup>2</sup> Austin, *loc. cit.*, p. 412.

observed that, when increasing alternating voltages are applied, the rectified current is first in the direction of the thermoelectric current due simply to heating the contact; then, with increasing voltage, the current becomes reversed. The contact here is not extremely small, and the results suggest that a certain amount of heating is necessary before the asymmetric condition becomes established.

It has been shown,<sup>1</sup> that, with a ball-coherer, the potential difference across the coherer does not depend upon the pressure between the balls of which the coherer is made (within certain limits). In this case, the region *A*, Fig. 10, must be varied, and hence, as was assumed, the resistance must be smaller than that of *B* or *B'*.

There are, however, certain weak places in the theory. When the circuit is broken, the heated contacts should cool very rapidly, and the resistance should return promptly to its initial value. To account for the facts, it must be assumed, then, that the ions can diffuse, more and more slowly, in the solid substance of the cold particles, as the asymmetric condition changes for some time after opening the circuit—thereafter remaining constant for hours. The diffusion would, of course, be in such a direction as to equalize the distribution of the ions.

It is difficult to account for the re-coherence of two copper wires, unless there is initially a semi-solid film on the surface of the copper, and ions become more or less permanently entrapped in this film—which, in part, constitutes *B* and *B'* in the figure—and only slowly diffuse therefrom.

Guthe and Trowbridge<sup>1</sup> in explaining the critical voltage of the ball-coherer considered that, as the current is increased, the area of contact remains constant until the current rises to such a value that a certain maximum number of ions cross the area. If the current be increased beyond this value, the effective area is increased by ions filling up the space exterior to the original area. The theory of asymmetry, then, explains critical voltage of the ball-coherer if it is considered that the region *A* spreads out on sufficient increase of current.

With balls of different metals, the critical voltage is independent of the direction of the current, but may be less or greater than the

<sup>1</sup> Guthe and Trowbridge, *loc. cit.*, p. 421.

critical voltage of either. This is difficult to explain unless it is supposed that the atoms of the two metals cross the film and combine, during the transit, to form a single ion.

#### SUMMARY.

(a) In general, when an E.M.F. was applied to a powder, or to the solids AgI, BaS, and molybdenite, the conductivity fell, rapidly at first, finally approaching a limiting value. If, after the exposure to the E.M.F., the circuit were broken, the conductivity tended to regain its original value, rapidly at first, then more and more slowly.

In some cases, *e. g.*, with molybdenite, the conductivity rose on application of the E.M.F. In other, still fewer, cases, *e. g.*, with BaF, the conductivity remained constant.

These changes were occasionally (but rarely) reversed in an unaccountable way.

With powdered BaS, the conductivity rose, apparently spontaneously after the substance was powdered.

(b) While the changes under (a) were taking place, the conductivity was found to be changing in the direction opposite to that in which the current originally flowed, the rates of change of conductivity in the two directions being, in general, opposite at any time; but only in the case of solid AgI were they of the same magnitude. Solid molybdenite alone gave a large permanent difference of conductivity.

(c) With all the substances examined, except powdered zinc perborate, the current did not increase in proportion to the E.M.F.; *i. e.*, Ohm's law was not obeyed. The  $E$ - $I$  curve was always concave toward the  $I$ -axis, becoming linear in some cases, for the higher E.M.F.'s. This latter type of curve has already been found to hold for the coherer.

The deviation from Ohm's law was present in all circumstances except under the application of great pressure.

(d) The effect of a vacuum was much the same for all substances examined. When the vacuum was produced, the conductivity fell considerably; rapidly at first, and then slowly. This fall took place with or without the current flowing, and whether the E.M.F. had been applied for a long or a short time, preceding the vacuum.

After the admission of air, the conductivity rose, in general, slowly and at a constant rate.

(*e*) All these effects were independent of the particular metal between which the substances were placed. Stirring or jarring a powder brought it more or less closely to the condition that held before the E.M.F. had been applied.

Finally a theory depending on slow diffusion of ions in heated contacts between particles is offered in explanation of the above facts.

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