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**A STUDY OF THE CONDUCTIVITY OF SELENIUM
AND ALLIED ANOMALOUS CONDUCTORS.**

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INTRODUCTION.

At the very beginning of the work herein described, the aim was to study the resistance of selenium under various conditions, but the work gradually expanded into a study of the conductivity of selenium, phosphorescent substances, and thence to that of powders in general.

THE CONDUCTIVITY OF SELENIUM.

The selenium cell,—sometimes called the selenium bridge, since it consists simply of a piece of selenium of any form between two wires so that a current can be sent through it—has been extensively investigated by numerous physicists, those having done most important work being Rukmer, Shrott and Robert Marc.* All have studied the changes in resistance produced by light under various conditions.

An electrical effect has been discovered with selenium by two Italian investigators, Pochettino and Trabacchi. They found that if an alternating E.M.F. be applied to a piece of selenium the resistance is found to be different after the application, and this change may persist for hours or even days, the original value of the resistance finally being attained.

* For reference to articles read in connection with work on this thesis, see bibliography at the end of the paper.

It has been found that there are two forms of selenium, of different conductivities, which exist in an equilibrium mixture when together. Physical agents, such as heat and light, displace the equilibrium in one direction or the other, thus altering the resistance. The color of the selenium has an important bearing, and this has also been studied. Of course the discovery that selenium, in its sensitiveness to light undergoes allotropic transformation and obeys the mass law is important, but it is by no means a complete explanation. The fundamental question is how the light alters the atomic or molecular forces so as to produce this change; but this question involves the discovery of just how the light alters the atomic or molecular forces so as to produce this change, which is a more difficult matter.

THE ELECTRICAL EFFECT IN SELENIUM.

The electrical effect in selenium, i.e. the effect of charges and currents on the resistance, has not been investigated to any extent except by Pochettino and Trabacchi, who offered no explanation.

During the course of the preliminary experiments, a cell of German manufacture was found to give the reverse effect to that discovered by the Italians. They found that when an alternating current or discharge was passed through a cell, the current first fell, then after the alternating current was removed, rose above the original value, and thereafter fell slowly.

The cell used by the writer was a round, Ruhmer type of cell, with a resistance close to 100,000 ohms. It consisted of a hard rubber cylinder on which was a fine double thread. In each thread ran a very fine copper wire, and over the surface of the cylinder was a thin layer of selenium. This cylinder was enclosed in an exhausted cylindrical glass tube, made to fit an incandescent lamp socket. The electrical effect observed was that produced by connecting both wires from the cell to one pole of an electric machine, and two narrow strips of tin-foil on the outside of the glass cylinder to the other pole. Paraffine was melted and run over the socket to insulate it from the tin-foil.

It was found that the resistance fell on causing sparks to pass at the terminals of the machine, the resistance afterward slowly rising to its original value. This is strictly analogous to the light effect, as may be seen from curves A and B, Plate I. The ordinates are the deflections, and the abscissae, the time. The deflections throughout the paper are the actual deflections, corrected for the zero.

The electrical and light effects together gave simply the sum of the separate effects. The effect was not changed by shifting the wires at the poles of the electric machine. The application of 220 volts A.C. gave a change in resistance of about one per cent., but here there was a rising, followed by a falling off in resistance. A steady field gave no effect; neither did connecting the tin-foil alone or the cell alone to one pole of the machine. On the other

hand, a single spark at the machine gave a noticeable effect.

A cell was then constructed and mounted between two glass plates, held $1/16$ " apart by glass strips, the edges being sealed with wax except at one point where a small tube allowed the receptacle to be exhausted. Strips of tin-foil were fixed to the outside of the plates.

The cell was made by winding two platinum wires a short distance apart around a piece of mica about one cm. square, covering one side with melted selenium and allowing the cell to remain in a paraffine bath at 200° for about three hours, afterward cooling it slowly.

Steady fields were applied for a minute or more by steps of 500 volts up to 10,000 volts, but no effect was observed. It was found, also, that there was no change in the resistance when a constant high difference of potential was maintained between the cell and both plates together.

A change in resistance, did, however, occur when either the tin-foil disks were connected to the poles of the electric machine, or the cell and one disk was connected to one pole, and the other disk to the other pole, and sparks passed at the terminals of the machine. In the former case the resistance rose during the time of the discharge - just opposite to the Ruhmer cell first used - and then fell to a value less than the original resistance, there being a permanent decrease in resistance after the experiment. This is precisely the effect referred to above, observed by the Italians. In the latter

case, with the cell forming one plate of the condenser, the rise was not so great, and the fall greater. There seemed to be a slightly greater fall when no current from the battery flowed through the cell in this second case, but the change was so small as to make it uncertain.

The curves representing changes with and without the vacuum can be seen in curves C, D, E and F, Plate I. It was found that a steady field had no effect in the vacuum, as at ordinary pressure. The vacuum was produced by an oil pump, but was not very high.

The change in the electrical effect produced by the vacuum may safely be ascribed to the conductivity of the vacuum. The vacuum in the Ruhmer tube was probably rather high, and as the two wires were but a short distance apart, bridged across with selenium, the residual ions in the gas after the discharge probably made the space outside the selenium a better conductor than the element itself, and more than counterbalanced any electrical effect of increased resistance.

The small change shown by curve E, for the vacuum produced by the oil pump, is probably due to the fact that the discharge, in passing through the vacuum between the outer tin-foil plates, chose the vacuum around the cell as an easier path than the path through the cell itself, and hence the electrical effect due to currents in the selenium was smaller than for the other cases, where the current flowed through the selenium.

ATTEMPTS TO MAKE A SILVER IODIDE CELL.

Hermann Scholl, "Ann. der Physik," 16, p. 198, has studied at considerable length the electrical properties of films of moist silver iodide. He concludes that the silver iodide, as such, is an almost perfect insulator. In the ordinary solid form it is crystalline, and full of minute cracks. When placed in an electrolyte, the liquid fills these cracks and conduction takes place in them. The effect of light is rather complex. It causes electrons to be given off, iodine to be liberated, and the formation of a new substance. Ions diffuse through the film with a speed several times greater than that of the fastest electrolytic ions.

An attempt was made to render the silver iodide conducting without having to resort to solutions of electrolytes, in order that the production of electrons, and hence of static charges, by light could be studied. About a dozen cells were made, melting the iodide with finely divided silver, heating the iodide until it decomposed slightly, yielding free silver, and melting the iodide which had been previously moistened with a weak solution of silver nitrate. The mixture was in all cases melted on glass between two platinum wires which served as electrodes.

It was found easy to make the iodide a sufficiently good conductor to enable the resistance to be measured easily. The source of light was a Nernst lamp.

The light effect was very uncertain. Sometimes there was a small apparent decrease of resistance, but in all cases where the change was at all marked the effect was due to heating. This was proved by holding a Bunsen burner near the cells and making it alternately luminous and non-luminous.

It is probable, then, that, although there may be a change of substance when light strikes silver iodide, the giving off of electrons is associated with the electrolytic action.

A curious effect, not produced by light, was noticed. The resistance of some cells increased while the current flowed. The deflection with one cell fell from 70 to 62.5 in 4.5 minutes, and thence to 42.5 in 8 minutes more. Another fell from 26 to 17.5 in 2.5 minutes, and then remained there fairly steadily 17 minutes.

In view of what was found later, these facts are significant.

THE RESISTANCE OF CALCIUM SULPHIDE AND OF POWDERS IN GENERAL.

After a phosphorescent body is exposed to light, it becomes self luminous, the intensity of the light given out gradually falling off. Selenium, on the other hand, becomes a better conductor after exposure to light, the conductivity gradually falling back to the original value. Nichols and Merritt have found that the curves

showing the relation between intensity of the light given out by phosphorescent substance, with time are very similar to those representing the decrease of conductivity of selenium with time. This similarity suggested that there should be, by analogy, a change of resistance in phosphorescent bodies on exposure to light. This seemed all the more probable when it was considered that phosphorescence is most likely due to molecular breaking down and rebuilding.

The first cell to determine the presence of such a resistance change was made by placing a small quantity of calcium sulphide, in the form of a very fine powder, between two strips of tin-foil about 2" square, one of which had slits cut in it to allow the light to diffuse into as much of the substance as possible, the whole being pressed between two glass plates.

The resistance is so high that a battery of 20 storage cells, each supplying two volts, was necessary to give a good deflection. A change of pressure increased the conductivity very markedly.

No light effect could be detected, but a very curious electrical effect was noticed from the first. Under all conditions it was found that the deflection, large at first, fell rapidly and then more slowly - a steady value not being reached until after a considerable time.

For example, the cell, after some trials, had at 3 P.M. a resistance such that the deflection was 22.8. During the course of the afternoon it fell to 12.5.

Three days later at noon, it was 3.8. The current was removed, and readings were only taken at long intervals. The change with time was as follows:

1 P.M.	20 cells,	25.5 divisions
3 P.M.	20 "	34.0 "
4 P.M.	20 "	43.6 "
5 P.M.	20 "	69.3 "
10.30 A.M.	5 "	52.0 "

It is seen that 20 cells gave about 3 divisions, while the next day 5 cells gave 45 divisions. Hence the decrease of resistance was approximately 60 times.

A more satisfactory cell for testing the light effect was then made as follows: twelve strips $3/16$ " wide and 4" long were cut from sheet zinc. The edges were smoothed with a file, and the strips were then placed upon a piece of glass, as near together as possible without touching - this being done with the aid of a microscope. The powdered CaS was sprinkled over these slits, and another piece of glass clamped over the first. With this cell, any light effect occurred at the places of greatest current density, and hence ought to have produced the most marked effect.

It was found, however, that little or no light effect could be detected even with this cell. An effect was observed when a piece of violet glass was placed over the cell with a Nernst lamp about 10 cm. from it, but as it was found that such a piece of glass at this

distance from the lamp became considerable heated, the effect must have been due to heating. The light was then passed through 4" of water containing a blue violet ammoniacal copper salt. The sulphide became phosphorescent, but the increase in deflection, only one or two divisions could be more than accounted for by the shift of the zero that was observed.

Hence, if any light effect is produced, it is very much smaller than the electrical effect. This does not preclude the possibility of such an effect, for if the resistance of a powder is almost entirely contact resistance between particles a change in the bodily resistance will be completely masked.

This cell, after the resistance had increased to a steady value, was connected across the terminals of a small induction coil. This had the effect of greatly decreasing the resistance, which, however, soon rose again as an E.M.F. was applied.

EFFECTS OF ALTERNATING CURRENTS OF LOW PERIOD.

To study the electrical effect more completely a new cell was constructed. Two flat copper disks from a Drude's wave apparatus, about 5" in diameter, were used as electrodes. The powder was sprinkled between them to form a thin layer, a silk thread being placed around the edge of the plates, between them, to prevent contact at the edges. The disks, with a weight on top, were placed on a bracket.

The resistance of this cell was so low that only 11 cells were needed to give a good deflection. A Pohl's commutator was arranged so that the current through the cell could be reversed without changing that through the galvanometer. A key was pressed when this shift was made to avoid short-circuiting the galvanometer through twenty odd volts.

For convenience, one direction of the current is called A and the other B.

On applying the E.M.F. the deflections, at first very large, decreased for both A and B.

When A and B were both 15 (made so by proper reversing) the current was shifted every 3 seconds for 1 minute. At the end of this time, B had risen to 20.5. It still rose until after 3 minutes it was 22.5, after which it began to fall. At this point A was 24.5, but on keeping the circuit closed it fell to 19.5 in 1.5 minutes.

When A and B were both 16, the operation was repeated, except the reversals were 1 second apart. After this, B rose from 17 to 20 in 3.5 minutes.

The same thing was then tried for A. Reversals were made every 3 seconds for 1.5 minutes. A rose from 12 to 13.7 during this time, and in 5 minutes afterward had risen to 14.7.

It should be noted that for both A and B, the deflections were falling before the alternations were performed.

The next day the same experiments with the cell were continued with a slightly different result.

At first 5 cells gave a deflection of about 30, showing that the resistance had fallen since the night before — the last readings taken being A 14.7; B 17.6.

Trying the alternating current as before, for 1.5 minutes, 10 second period, B changed from 15.3 to 11.5, then rose to 13.7 in the following 5.5 minutes. The same thing repeated when the deflection was 11.7 with a 5 second period, changed it to 10. It then rose to 11.8 in 5.5 minutes, where it remained for about 1 minute.

With a 2-second period, it changed from 11.2 to 10.7, and then rose to 11.7 in twenty minutes.

With B, for a $1/4$ -second period, B fell from 9.7 to 9.3 thence to 9.0 and rose then to 10.9 in 17 minutes.

The shorter the period, then, the greater is the length of time of the rise.

During the course of the experiments the calcium sulphide cell was short-circuited through the galvanometer, but no E.M.F. or polarization could be detected at any time.

It should be noted that when the alternations were but a fraction of a second apart, an appreciable time elapsed between successive contacts, and this might have had an influence upon the readings, as the change in resistance produced by the opening of the circuit is opposite to that resulting from the alternations.

Curves characteristic of the results obtained on the two days in question are given in Plate 2, A and B. Both of these are similar to those obtained by representing graphically the electrical effect in selenium. The curve

B is especially similar to the curves given by Pochettino and Trabacchi showing the electrical effect in selenium for alternations of 60 cycles per second at convenient voltage.

. CHANGES OF RESISTANCE AS THE CURRENT FLOWS.

Closely connected with the effect of alternating currents is the effect of reversals in general. The growth of conductance in the opposite direction as the current is sent constantly in one direction was observed as follows: the current was kept constantly in the direction A, and reversals (i.e., B) were made at intervals of two minutes, only long enough to take a reading. It was found that as the deflection for A, which had become steady, kept nearly constantly at 2.1, the deflections for B increased gradually from 5.7 to 9.5 in 17 minutes. Then the current was shifted to the direction B, and A was taken quickly at intervals. B. fell slowly from 3.4 to 2.8 in 29 minutes, and then remained fairly steady up to the time the experiment was stopped at 25 minutes later, while A rose steadily from 11.5 to 15.3.

This shows that when the current flows steadily there is a decrease of resistance in the opposite direction.

CHANGE IN RESISTANCE AFTER OPENING THE CIRCUIT.

Immediately after the last experiment was performed, the circuit was opened, and readings were taken at two-minute intervals of first B, then A, closing the circuit

for as short a time as possible. The deflection for A fell from 14.8 to 8.8 in 22 minutes, while B kept at about 3.2. The deflection for A reached a steady value quickly. For B, however, the first throws grew larger and larger until they reached 8 or 9, falling rather rapidly to about 3.2. In this case, then, the resistance increased at least at first, on opening the circuit.

DEVIATION FROM OHM'S LAW.

As has been said, the resistance of powdered CaS increases slower and slower with time until a steady value is reached. The number of storage battery cells in circuit was changed after such a steady value had been attained, and it was found that the deflection was not proportional to the number of cells in series with the galvanometer and the CaS cell; i.e. the current was not proportional to the voltage. If the voltage was changed only long enough to take a reading, such a set of readings could be taken without altering the steady value of the resistance mentioned above, and, moreover, the same readings were obtained when the current was reversed and the voltage changed in the same way.

So far as could be learned, this was a new effect, and the remainder of the time was spent in trying to determine the cause. Hitherto experiments have been made with powders only to determine the specific resistance of the chemical compounds, and for this purpose the powders were all highly compressed. This, as will be shown,

destroys the deviation from Ohm's law.

An attempt was first made to determine the effect of thickness on the conductivity, other conditions being the same. A cell was constructed of three glass plates. Upon each of the pairs of surfaces in contact well flattened pieces of tin-foil, all of the same area, were made to adhere by the application of a little universal wax to the surface of the glass. This gave two cells. A layer of CaS of uniform thickness was made by placing metal strips on each side of the foil, sprinkling the powder over the foil, and taking off the surplus by moving a straight-edge along the metal strips. In this way two layers of different thicknesses, each a fraction of a millimeter, were made. A heavy weight was placed on the cell.

The voltage was adjusted so that the same deflection was produced for each cell, namely 85. The voltages were 20 and 40 respectively. The deflections kept much the same for three quarters of an hour. Then the deflection of the thin cell was observed to be falling faster, so that for the final steady value, it was about half the deflection of the thick cell.

This suggests that the resistance is first only a body resistance and finally only a surface contact resistance, but it should be borne in mind that as Ohm's law is not fulfilled, it is unsatisfactory to predict by Ohm's law what the effect of thickness should be. Another experiment with two different thicknesses gave a less intelligible result even than this.

Curves are given, C and D, Plate 2, showing the deviation from Ohm's law at the beginning and end of the experiment. The curves are evidently changed in steepness, but not in form.

SPECIFIC RESISTANCE OF POWDERED CALCIUM SULPHIDE.

With the above pair of cells it was possible to measure the specific resistance of powdered CaS . The thickness of the layers of CaS were found by making a number of measurements across the glass plates before and after removing the CaS . The mean thicknesses were 0.23 m/m and 0.674 m/m. The galvanometer constant was found in the usual way from the deflection produced by a known, very small, difference of potential across the terminals of the galvanometer, knowing the galvanometer resistance, and noting the deflection. The constant was 2.5×10^{-7} . The specific resistances of the thick and thin layers, for the steady value, were found to be 1.87×10^7 and 1.56×10^7 ohms, respectively.

CALIBRATION CURVE.

In order to eliminate error due to the deflection of the galvanometer not being proportional to the current, the galvanometer was calibrated, by tapping off from a 100 cm. slide wire in series with a high resistance, thus enabling equal increments of potential to be taken across the galvanometer. The calibration curve is given as E,

Plate 2, and may be compared with the subsequent curves. three days. At the end of that time the resistance was measured, and it was found to be the same as if the cell

EFFECT OF PRESSURE.

Since no deviation from Ohm's law has been noticed in solid sulphides, it is evident that under great pressure, a powder must conform more closely to the law. This was found to be the case. Curves between current and E.M.F. are shown in Plate 3. A was obtained before any pressure whatever had been applied. B was obtained after a slight pressure with the finger, and C and D were obtained by pressing with a small clamp, D being taken with the greater pressure.

A heavy press, used for making pellets for a bomb calorimeter was next used, and the curves for this are given as E, F, and G. G is seen to obey Ohm's law very closely, and was for the greatest pressure. Curve H was obtained from the same specimen after releasing the pressure. With the second press, the pressure was applied to all the powder between the plates, and not to a portion of it, as was the case with the smaller press.

EFFECT DUE TO CHANGES THROUGHOUT THE MASS.

A number of attempts were made to determine whether the change of resistance was a body or a surface effect. It was concluded that the effect was due either to a change within the substance, or to changes in the surfaces between adjoining particles - more likely the latter.

Some CaS was placed between clean copper plates for three days. At the end of that time the resistance was measured, and it was found to act precisely as if the cell had been freshly prepared, although there was a blue film of sulphide on each of the copper plates. To another such cell, 40 volts were applied for three days, but there was no perceptible difference between the plates at the end of that time.

Further experiments indicated that the effect arose from the contacts between particles. A cell was made with CaS between copper plates. When a steady deflection had been reached, it was found that with care, the upper plate could be removed, rubbed clean, and replaced without changing the deflection. This shows that the effect is not due to a film on the surface of the electrode. When an additional pressure was applied, the deflection increased falling again on release of pressure, but never quite to the initial deflection. A slight lateral movement of the upper electrode produced the same result. The deflection became large, however, if the upper plate were twisted; and the powder resumed its initial state when stirred before replacing the upper electrode.

No difference in the effects have been observed with copper, tin, zinc and platinum electrodes.

These experiments tend strongly to the conclusion that the resistance - time effect is a contact or coherer phenomenon.

DEVIATION WITH LARGE CURRENTS.

Some of the curves for CaS seemed to suggest that a straight line would be approached if the voltage were made considerably higher. The true state of affairs was found to be not so simple. A very thin layer of CaS was placed between two copper plates, so thin that a single cell gave as great a deflection as six or seven cells with the thickness usually used. The galvanometer was shunted. It was found for currents even up to those demanding a $1/100$ shunt; i.e. 100 times as great as were usually used, the deviation from Ohm's law was still marked. When, however, as much as 60 or 80 volts were applied, the deflections finally grew large even with a $1/300$ shunt, and became very irregular, due, probably to internal fusions - doubling the E.M.F. causing no increase in deflection; increasing it three times, doubling the deflection; and increasing it four times, bringing it back to its first value. Even after this treatment, the deviation was still present for low voltages, and the powder, after the experiment, appeared the same as before, and was still phosphorescent.

DEVIATION FOR OTHER SUBSTANCES.

Up to this time the phosphorescent sulphide had been used exclusively. It was found that the pure sulphide gave just the same effect.

Powdered barium sulphide deviated from Ohm's law

and the current voltage curve is given in Plate 3, I. The conductivity rose as the current continued to flow; K, Plate 3.

Solid barium sulphide was found to deviate from Ohm's law also; J, Plate 3. The conductivity rose as the current continued to flow, as represented by L, Plate 3.

Strontium sulphide deviated slightly from Ohm's law; A, Plate 4, and the conductivity fell slowly with time.

Zinc sulphide deviated slightly at first, B, Plate 4, and the conductivity fell with time, C, Plate 4.

Zinc perborate followed Ohm's law closely, D, Plate 4, and the conductivity remained constant, although the substance was in the form of a very fine powder.

"Zinc dust" was found to be as poor a conductor as most of the powders used, due, doubtless, to the covering of zinc oxide on each particle, although the amount of oxide present is but 6%. When tightly pressed in a tube in the form of a coherer, the curve was that shown by E, Plate 4. When placed in a thin layer between flat copper disks, the curve was that given by F, Plate 4. The conductivity fell with time.

Selenium deviated gradually from Ohm's law, but did not change in conductivity with time. Curve G, Plate 4, shows the deviation.

Barium carbonate deviated from Ohm's law, curve A, Plate 5, and the conductivity rose with time, curve B, resembling the rise for powdered BaS.

Barium sulphate did not obey Ohm's law, C and C¹, Plate 5, C¹ being obtained after passing the current through

for three days. The conductivity, however, fell with time, whereas with the other two barium salts it rose.

Barium fluoride deviated slightly, D, Plate 5, but the conductivity did not change appreciably with time.

Magnesium oxide, both as a pressed, and as a loose powder deviated from the law, E, Plate 5, and the conductivity fell with time, F, Plate 5.

Red iodide of mercury gave a deviation, different - as was the usual case - for increasing and decreasing increments of E.M.F., curve A, Plate 6. After applying the current for an hour, the two sets of points tended to coincide, B, Plate 6, as with CaS .

Black oxide of mercury showed little or no deviation from Ohm's law, C, Plate 6, but the conductivity fell fairly rapidly with time. This powder had, next to zinc dust, the highest conductivity.

Red oxide of mercury deviated considerably, D, Plate 6, and showed about as great a falling off of conductivity as the black oxide.

Mercurous chloride was of very high resistance, and at first only the throw of the galvanometer could be obtained with the cell as a condenser. Later, however, the current started to flow, but in the peculiar manner shown by E, Plate 6. There was probably some internal change produced by the current.

Calcium sulphate showed a slight deviation for low currents, F, Plate 6, and the conductivity fell with time.

One of the earlier silver iodide cells was tested

for Ohm's law. There was a slight deviation for low voltages, G, Plate 6, This silver iodide was in the form of a solid layer, and contained little silver.

Borax showed a deviation from Ohm's law, A, Plate 7, and the conductivity fell with time. On one occasion, however, the conductivity rose with time. Curve B_1 , Plate 7, was obtained after a two day run. Curve B_2 was taken 40 minutes after B_1 , leaving the current on meanwhile, except for the 10th minute, when by opening the circuit for a minute, the current rose three times.

Litharge showed a very small deviation, C Plate 7, but the conductivity fell to a third with the current flowing over night.

Black oxide of manganese was very irregular, due probably, to the breaking down of the granules under pressure, or possibly to slight fusions where the particles were crowded together. The grains were somewhat coarse.

A thin sheet of molybdenite between metal plates showed a deviation from Ohm's law, D, Plate 7. When the current was first sent through, the deflection was 23 divisions, by one cell, and for two it was off the scale; i.e. much greater than 100. Also the conductivity decreased after removal of the current, so that the current after 6 minutes had fallen to $1/8$ of its initial value.

A curious coherer effect was sometimes noticed with borax and barium sulphate when the 220 volt A.C. lighting circuit was opened or closed.

EFFECT OF MOISTURE.

In order to determine whether or not the effect was due to the presence of moisture, a quantity of Gas was placed on a piece of glass over water in a closed vessel for a day. The resistance was then measured, the galvanometer having first been shunted. Although the current was such that the galvanometer had to be used with the $1/1000$ shunt, there was still the deviation present, as may be seen by the curves E and F, Plate 7. The conductivity fell rapidly while the current was on. The next morning the deviation was only at the beginning of the curve, and a $1/10$ shunt was used. In the afternoon with a $1/3$ shunt, G, Plate 7, was obtained.

EFFECT OF DRYING THE Gas.

A small quantity of Gas was dried in a vacuum dessicator over H_2SO_4 . After four days it was removed, and was found, H, Plate 7, to deviate still from Ohm's law. When the current was applied constantly, the conductivity rose, I, Plate 7, but after the voltage was shifted this effect gave place to the fall of conductivity ordinarily observed. The effect, then, does not depend on dampness or dryness.

RISE OF CONDUCTIVITY WITH TIME.

The increase of conductivity with time appears to be due to the state of the powder, as it has been observed for other powders - once, in the case of borax. The similarity of the curves for this rise in different substances points toward similarity of form of powder rather than likeness of constitution.

It was found that a slight rise could be induced by applying a low E.M.F. after having just applied a high one. The rise was, however, small. With a fresh cell of Ba CO_3 , if the E.M.F. were kept constant there was a slight fall amounting to 1.5% in 10 minutes. On removing the E.M.F., the conductivity fell slightly. This could be repeated once or twice, even using a different voltage each time, but after that the conductivity rose slightly while the E.M.F. was applied.

EFFECT OF A VACUUM.

All the powders, and even the solid BaS give a large drop in conductivity in a vacuum, and a slow rise after the air has been admitted. The curves for CaS are given in A, B_1 , and B_2 which is a continuation of B_1 had using 5 cells, Plate 8. The effect of the vacuum on the deviation is shown by curves C, D, E, Plate 8.

C was taken after a 15 minute application of 7 cells.

When the lowest deflection with the vacuum had been

reached, D was taken, and immediately after admitting air,

C was taken. No rise in conductivity took place with a vacuum if leakage were prevented by constant pumping.

The curve for MgO is given as F, Plate 8.

The curves for solid and powdered BaS are A and B, Plate 9, respectively.

SPONTANEOUS RISE OF CONDUCTIVITY.

It was found that freshly powdered BaS rose greatly in conductivity spontaneously, rising to three times its conductivity in 3.5 minutes. The powder had a strong H_2S odor.

To investigate this effect further a sample of BaS was ground to powder and divided into two portions; one was allowed to remain open to the air of the room, and the other was placed in the vacuum dessicator, for 20 hours. At the end of that time the former powder rose slowly in conductivity, increasing $1/3$ in 20 minutes. It fell, however, when the current was steadily applied. The latter powder showed a falling conductivity, decreasing to about half in 2 minutes, still decreasing when the current was steadily applied. After several voltages had been applied for a few minutes, the deflection remained fairly constant for any particular voltage. This powder also had a strong odor of H_2S . The fall for fresh CaS was less than 6% for 3 minutes.

This is, of course, not strictly a spontaneous change, since a current has to be sent for an appreciable time to get even the first deflection. The effect is probably

due to a change resulting from short applications, and shows how the resistance-time effects are modified by previous history.

EFFECT OF LOW TEMPERATURE.

A cell was made of two glass plates, on which were strips of tin-foil, held together under compression with sealing wax. When the cell was immersed in a beaker containing ice and salt, the deflection fell greatly, as with the vacuum. On removing, it rose rather rapidly to a much higher value than the original deflection.

To eliminate the uncertainty due to a possible change in the compression of the powder, a cell was used of two large disks of copper placed on ice and salt. Here there was no change in the reading from that taken just before placing the cell on the mixture, the deflection ^{temporarily} first rising due to jar in moving the cell. On removing the ice and salt the deflection rose, curve C, Plate 9, showing that the rise is characteristic of the effect of warming immediately after cooling. Two days later the deflection was 6.7, curve C, Plate 9, showing that the resistance had ultimately risen.

EFFECT OF ELECTRO-STATIC FIELD.

It was found that there was no change in conductivity produced by electric fields either with or across the direction of the current that could not be accounted for completely by ordinary leakage currents.

SUMMARY OF EXPERIMENTAL RESULTS.

With a vacuum tube containing a selenium cell, of German manufacture, the resistance fell with an electric discharge. With a cell made for the experiment, the resistance first increased and then decreased, both with and without the vacuum.

A layer of fused silver iodide, containing a little silver, on glass gave practically no change in resistance on exposure to light, but the resistance of most cells of silver iodide increased while a current passed.

The resistance of calcium sulphide did not change appreciably on exposure to light, but increased as a current was passed through it, decreasing again to at least $1/60$ of its greatest value after the current was removed.

The effect of alternating currents of low frequency was to cause an increase of resistance while the current acted, this being followed by a decrease, the final value of the resistance being less than the original. The shorter the period of the alternations, the longer was the time of the decrease.

With the current flowing in one direction, even when the resistance for this direction was constant, the resistance was found to be decreasing in the opposite direction.

At least under certain conditions, the resistance increased in one direction after opening the circuit, at the same time remaining fairly constant in the other direction.

Calcium sulphide and a number of other powders, and even solid substances, BaS and AgI, did not obey Ohm's law, and the anomaly disappeared only when the substances were subjected to great pressure - moistening or drying, currents through a considerable range, and a vacuum not decreasing the effect.

A cell, when the current had been passed through long enough to give a constant resistance, could be disturbed to the extent of removing the upper plate or electrode, or moving it slightly laterally, without changing the resistance. Anything, however, that displaced the particles of powder relatively to one another produced a fall of resistance.

The resistance of powdered BaCO_3 and solid or powdered BaS decreased with time. That of all the other substances examined increased. This was not a hard and fast rule, as both phenomena were observed with the same powder, at different times.

Some substances showed both the deviation and the change of resistance with time; CaS, CaS, SrS, ZnS, BaCO_3 , BaSO_4 , MgO, HgO , CaSO , AgI, $\text{Na}_2\text{B}_4\text{O}_7$, and zinc dust.

Other substances showed but the deviation; Se and BaF. Still others showed only the change of resistance with time; HgO_2 , PbO . One powder, zinc perborate, showed neither effect.

A coherer effect was noticed with borax and barium sulphate when the 220 volt A.C. lighting circuit was opened or closed.

The resistance of some powders, notably BaS, changes rapidly after applying an E.M.F. for but a short time.

A vacuum, in all cases, produces a sudden increase of resistance. Readmission of air causes the resistance slowly to fall.

There is no appreciable effect upon the resistance of CaS when an electro-static field is maintained either with, or at right angles to, the direction of the current flowing through it.

SUMMARY OF SUGGESTED EXPLANATIONS.

1. An explanation that can be made to agree with most of the facts observed is that the effects are due to coherer action - fusion between particles in contact. This is supported by the resistance remaining constant if the particles are but little displaced from each other, and also by the high resistance of zinc dust, which is probably simply covered with a thin film of oxide. It is supported by the fact that the curves for rising conductivity are similar for widely different substances, and hence must depend only upon the form of the powder.

This does not explain, however, the effect of the vacuum, which, with some substances, would be more easily explained by supposing an ionized gas were given off. It may be simply a question of change of pressure on the particles in contact. Also, according to this supposition, the zinc perborate must adjust itself immediately to the E.M.F. applied, since, through a fine powder, it presents

no anomalies.

2. The resistance-time effect may be explained by supposing, as is probably the case, that there is intense local heating at the surfaces of the particles in contact, and that such heating either breaks or welds together the particles, thus increasing or decreasing the resistance. This receives some support from the recent theory of the temperature effect upon coherer action, that the small welded joints can stand a tension but not a compression, and hence an increase of temperature which might be produced by the joint itself, will make them decohere.

The case is probably not so simple as this, for an increase or a decrease in resistance can take place in the same substance - in fact, there seems to be a kind of unstable equilibrium as far as resistance is concerned. This must depend upon the state of the powder at a given instant, which, in turn, depends upon the previous history.

3. It must be supposed that electrolytical action of fused salts or other complex action takes place at the junctions between particles, to account for the decrease in resistance in one direction when the current flows in the other, and also for the increase of resistance after breaking the circuit under certain conditions. The effect of alternating currents probably involves this point, and the question may concern the phases a substance can assume at such points under high local heating.

4. The deviation from Ohm's law and the resistance-time effect cannot be fundamentally the same, as a sub-

stance may have either or both, and also because conditions which modify or reverse the latter have no effect on the former. Pressure alone removes it, and hence it may be a characteristic of powders and solids of certain structure. It is probably not due to alinement of the particles, since a strong electric field with the current does not increase the conductivity.

5. The effect noticed in solid BaS and AgI is probably due to contact resistance, as Scholl has shown that the latter is completely filled by a great number of very small cracks. It is difficult to arrive at another explanation. Under this supposition the electrical effect in selenium may be explained as due to contact resistance between groups of particles within the substance. The powdered selenium deviates from Ohm's law and thus presents anomalies in ordinary conduction, and, further, the curves for the alternating current contact resistance in CaS are almost identical with those for the electrical effect in selenium with alternating currents.

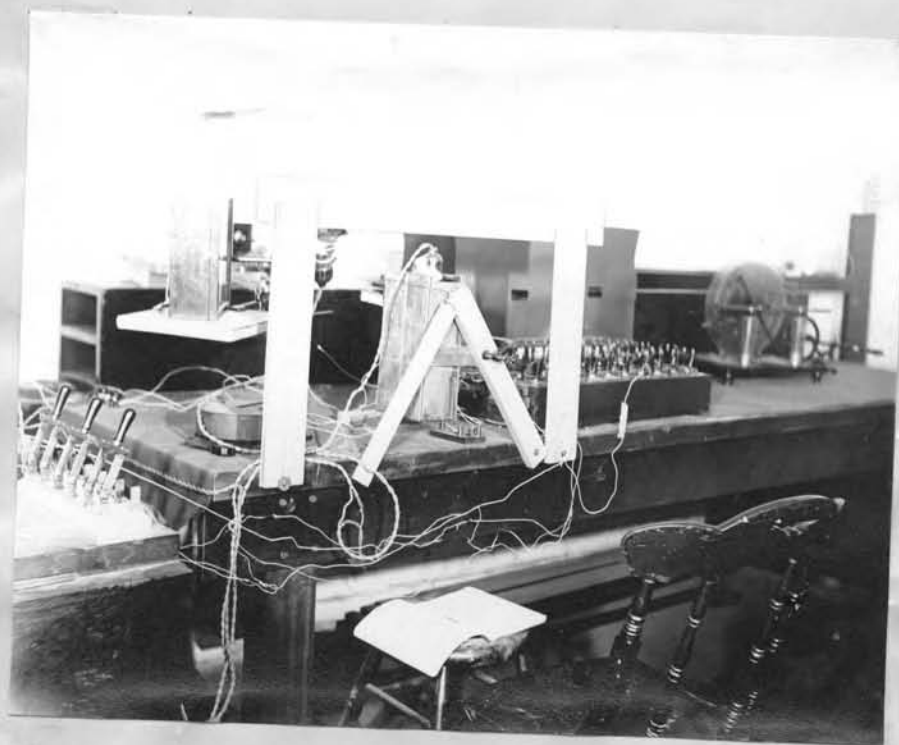
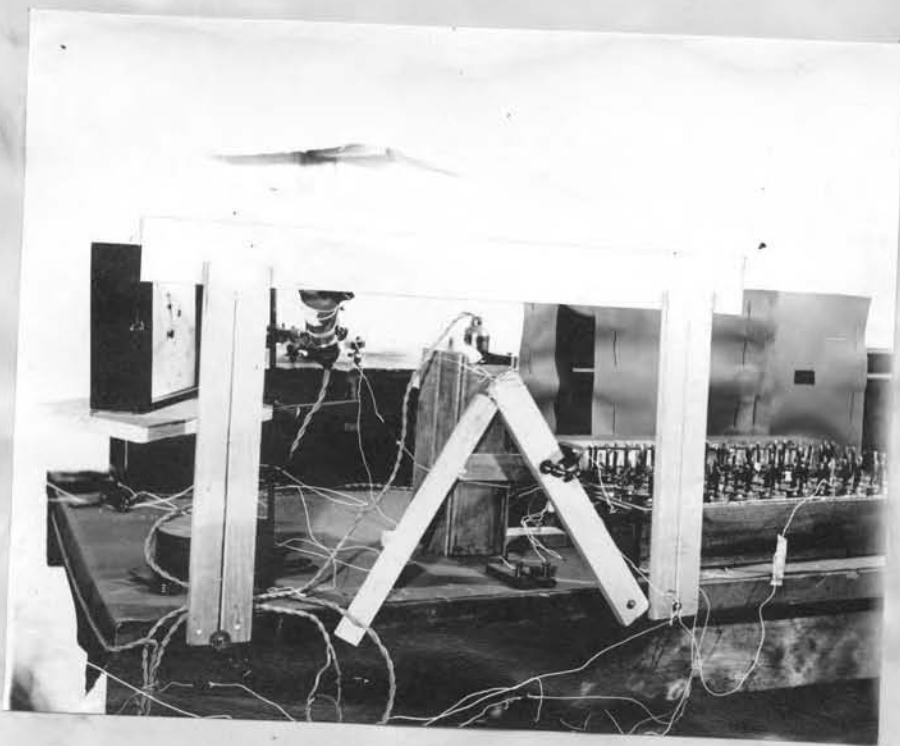
Of course these assumptions are but tentative, explaining some things well and others rather incompletely, but by modifying them to suit these exceptions, the actual conditions accompanying the passage of current in conductors which do not obey Ohm's law may possibly be determined.

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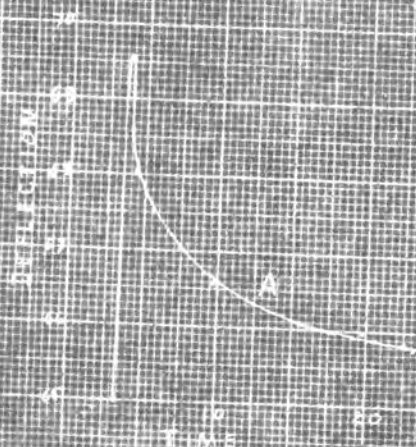
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ON SILVER IODIDE.

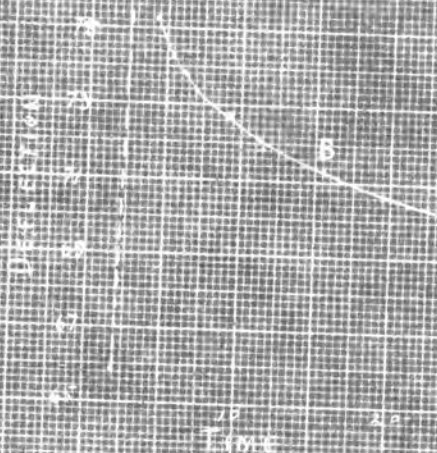
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SELENIUM

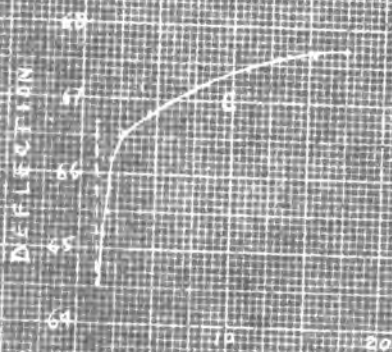


LIGHT EFFECT

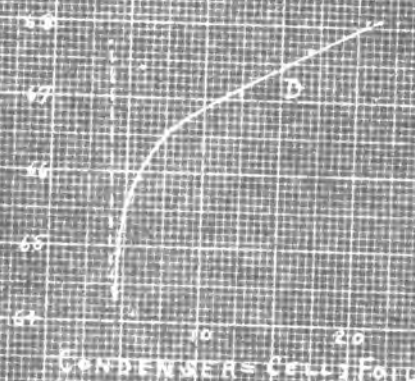


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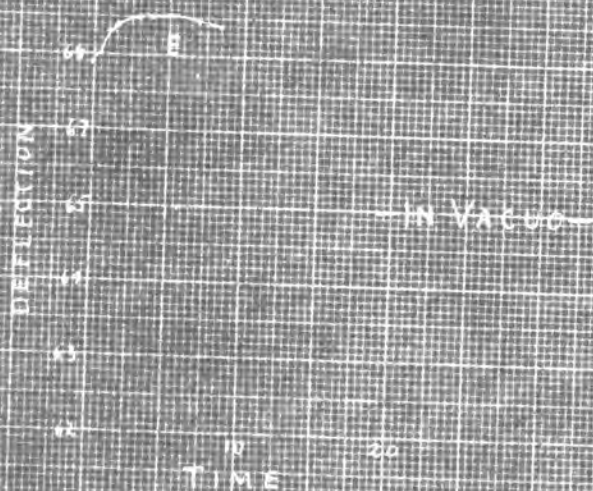
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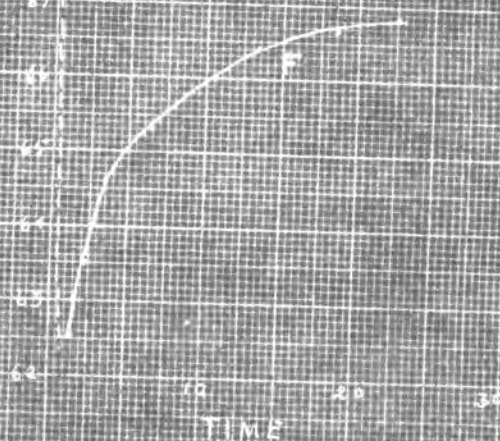
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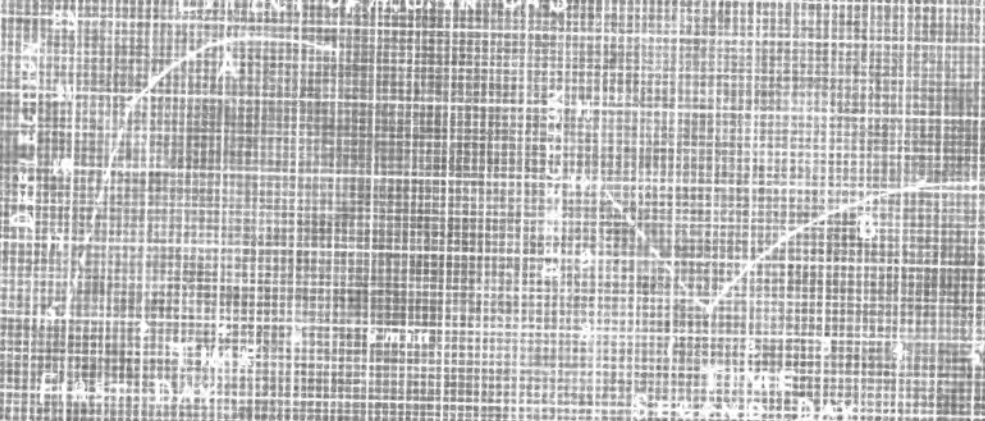
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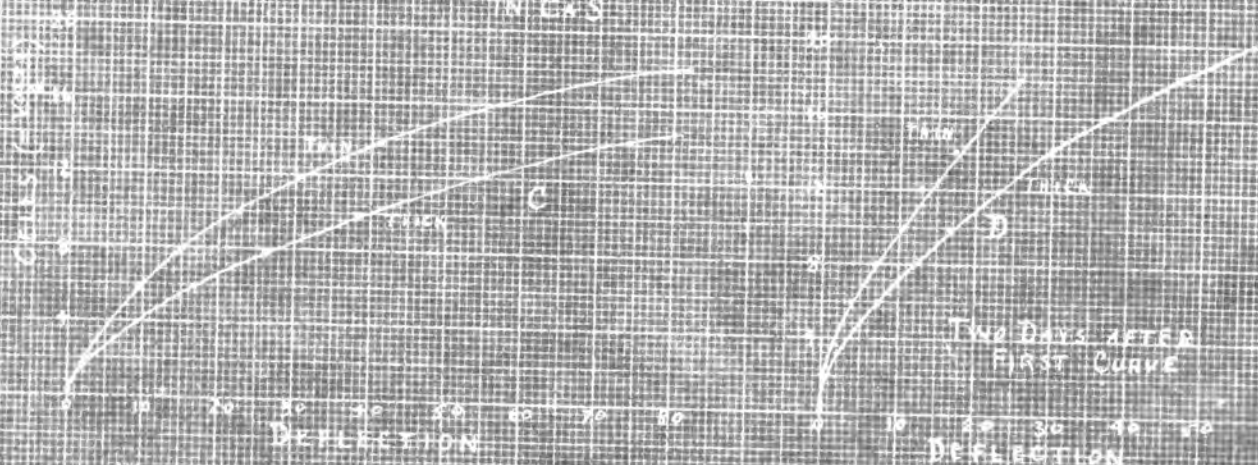
IN VACUUM



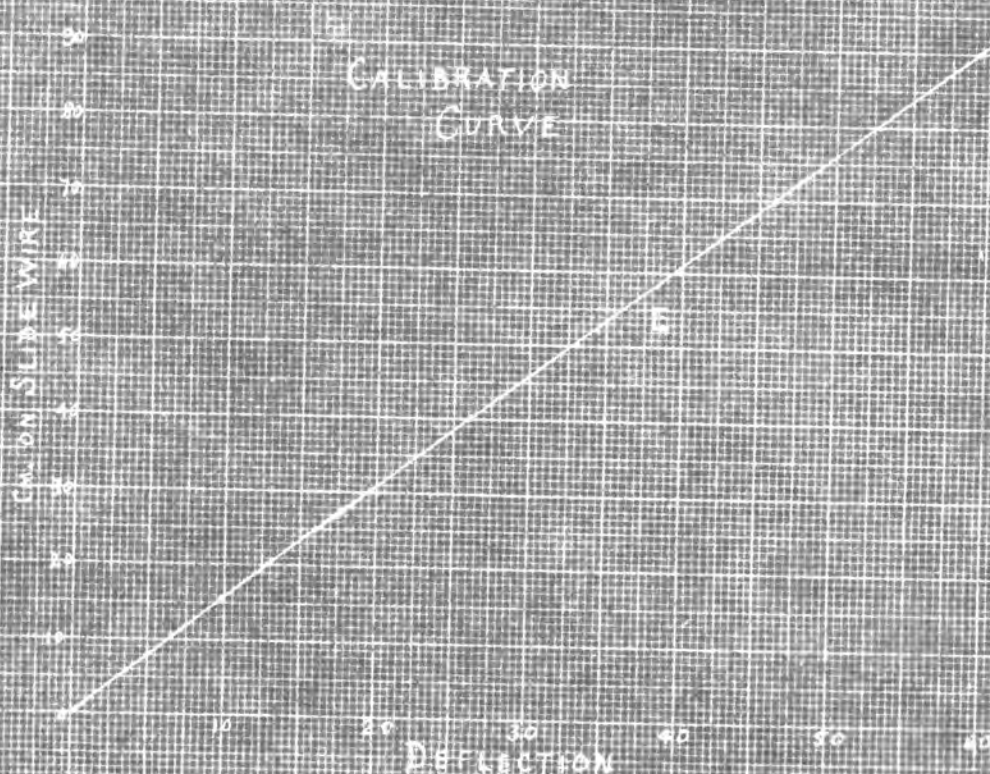
EFFECT OF A.C. IN GAS



DEVIATION FROM OHM'S LAW IN GAS



CALIBRATION CURVE



EFFECT OF PRESSURE ON DEVIATION OF GAS



PROPER SPECIMEN WITH GREATER PRESSURE

AFTER RELEASING

DEVIATION

CELLS

CELLS

SOLID GAS

POWDERED GAS

DEVIATION

DEVIATION

TIME

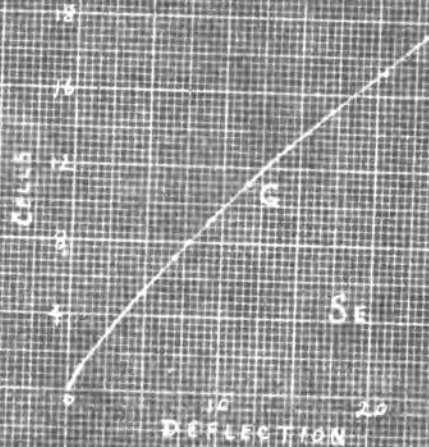
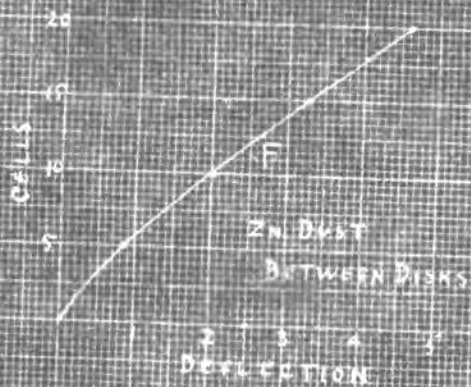
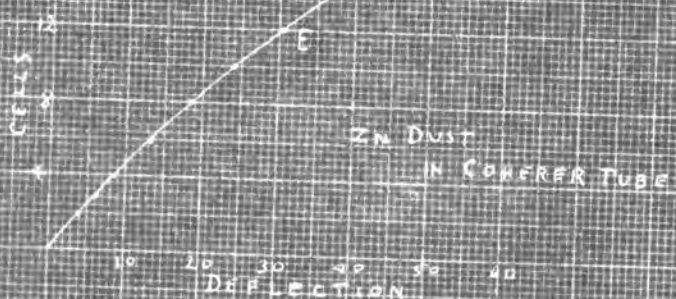
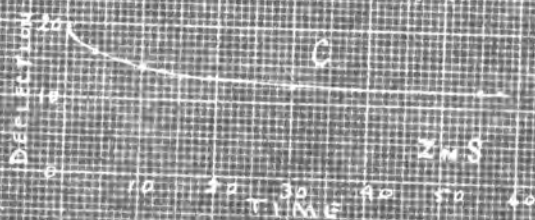
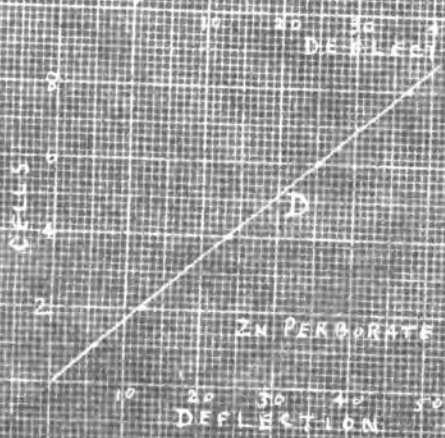
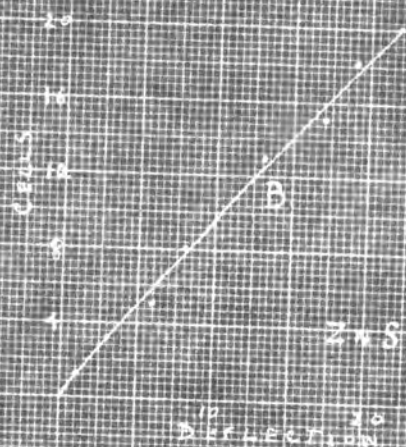
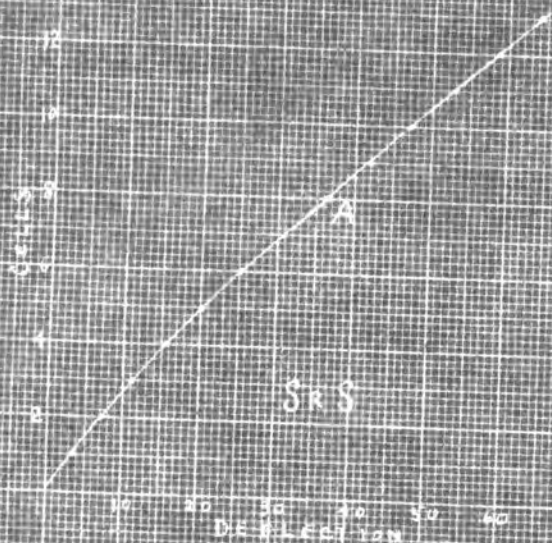
POWDERED GAS

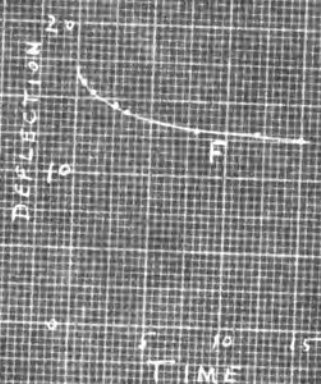
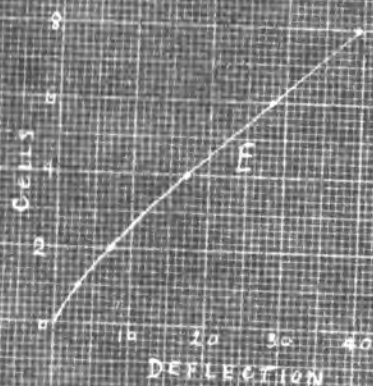
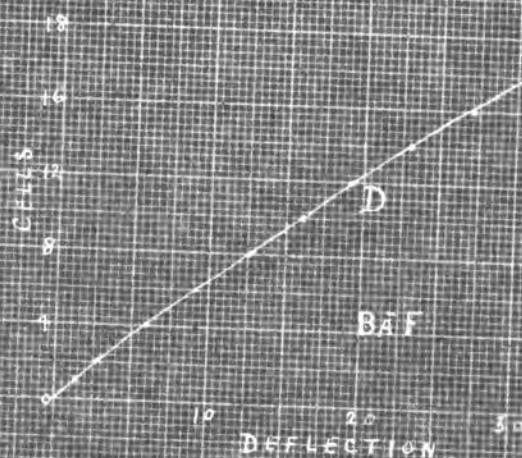
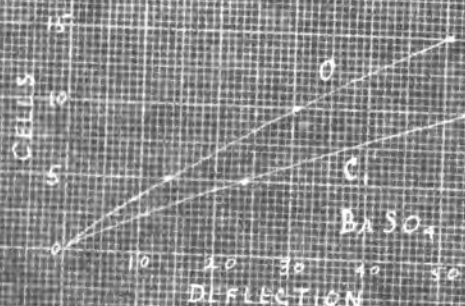
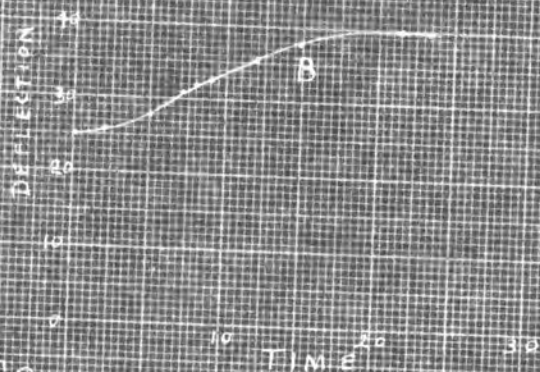
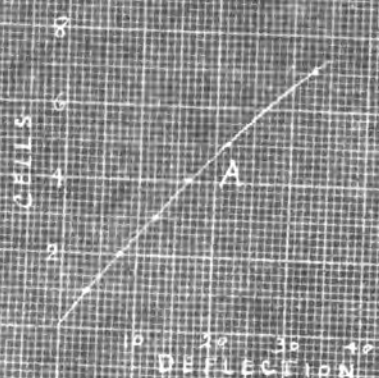
SOLID GAS

TIME

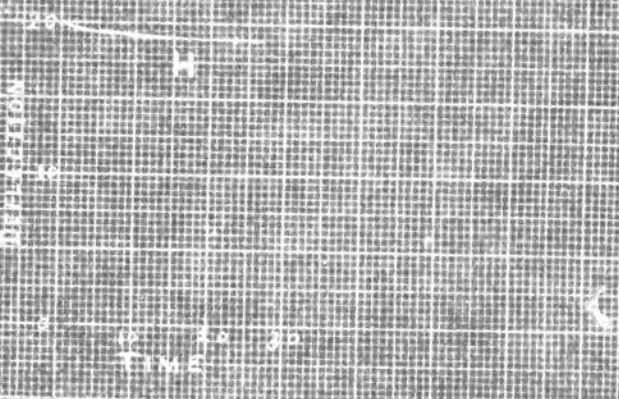
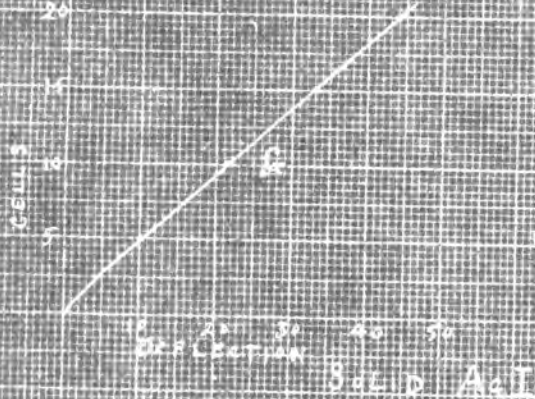
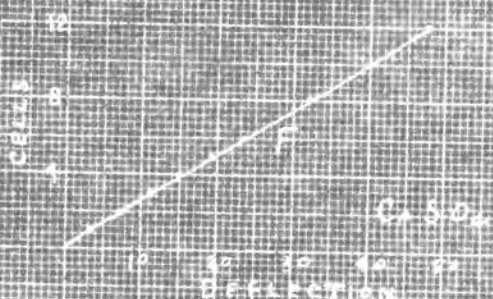
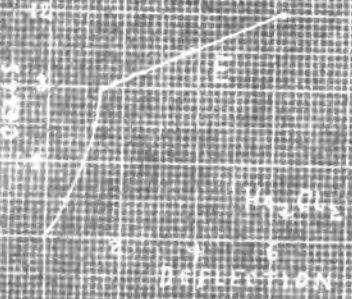
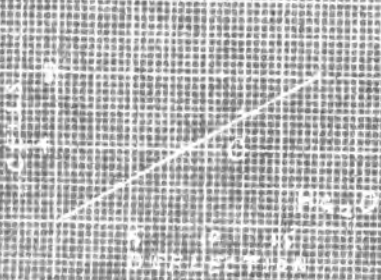
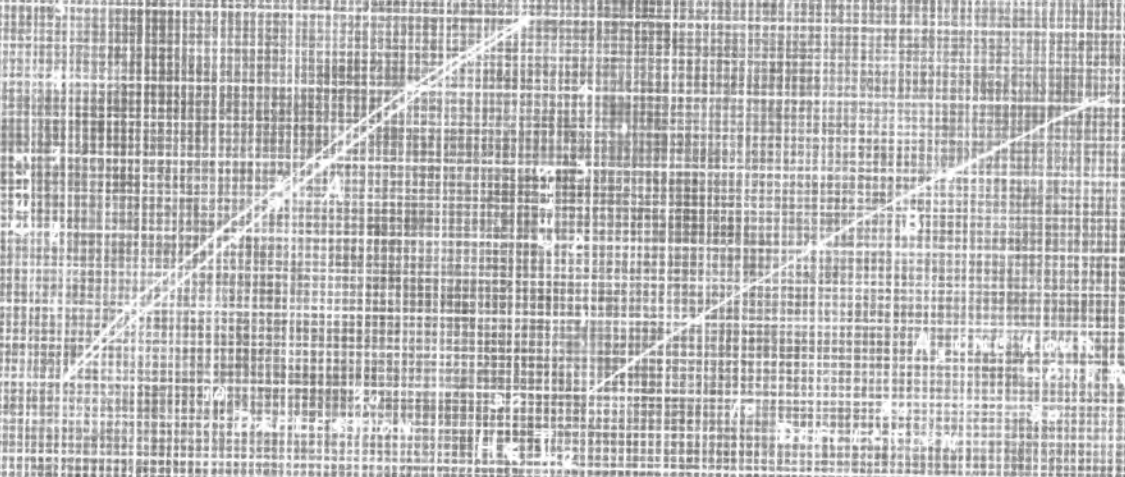
GAS

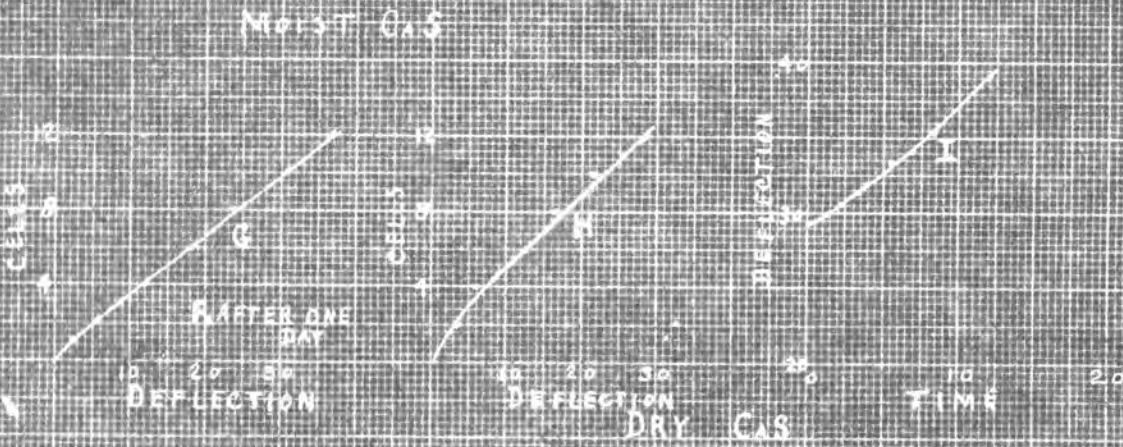
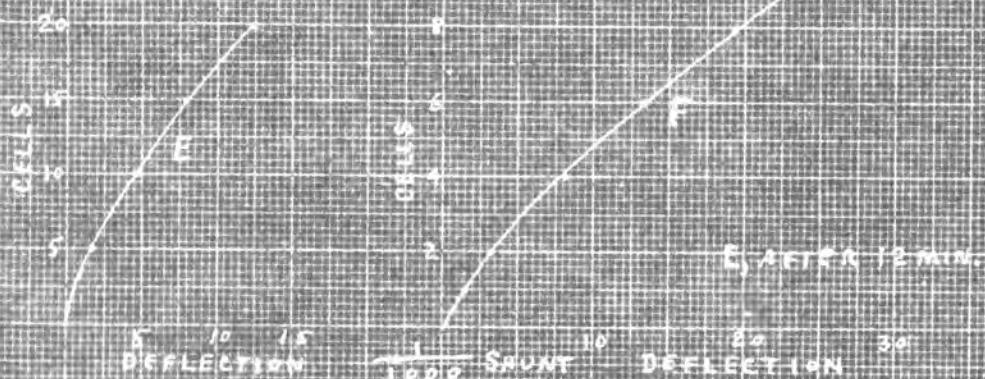
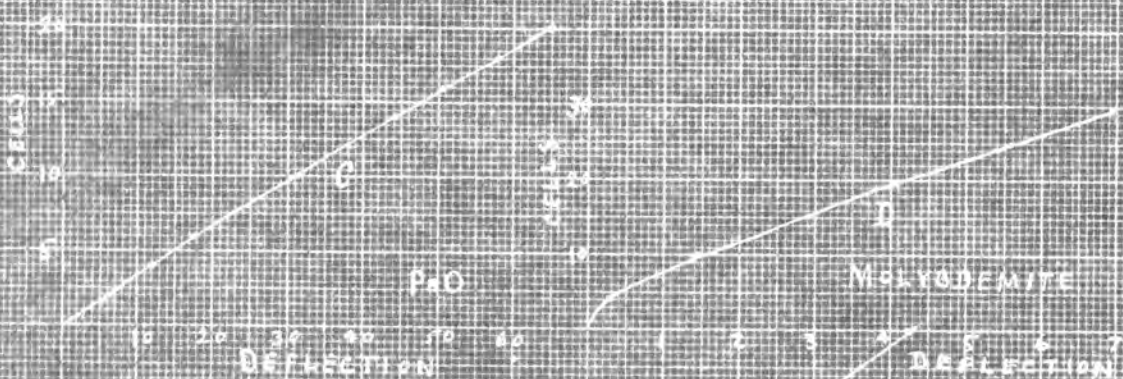
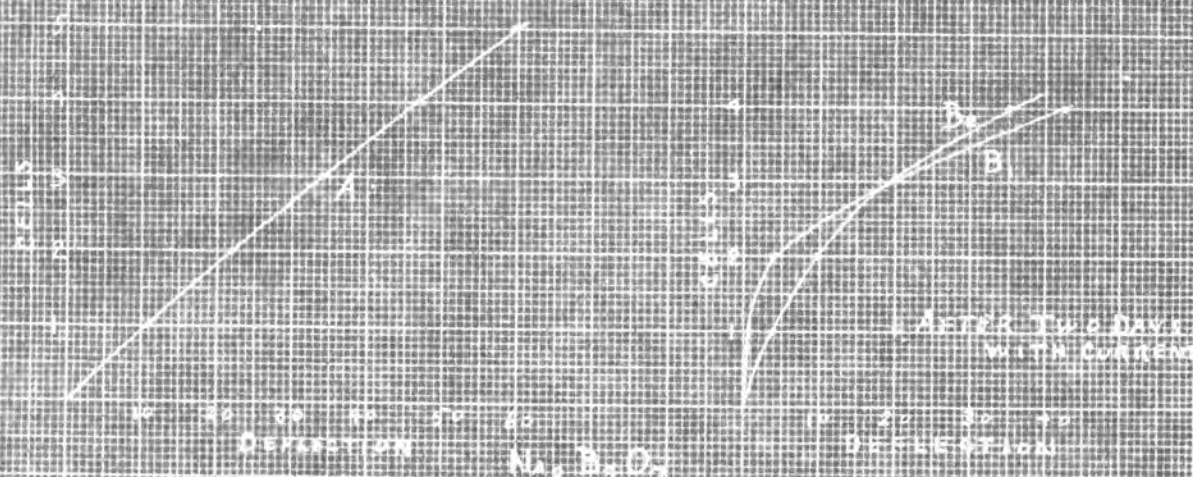
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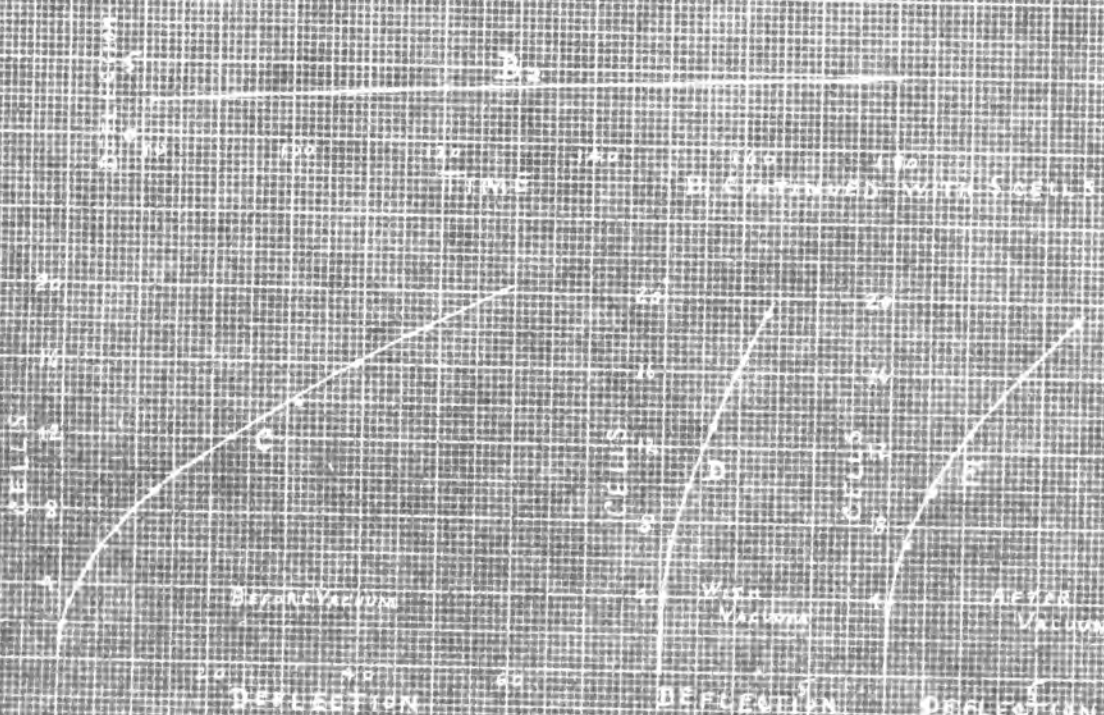
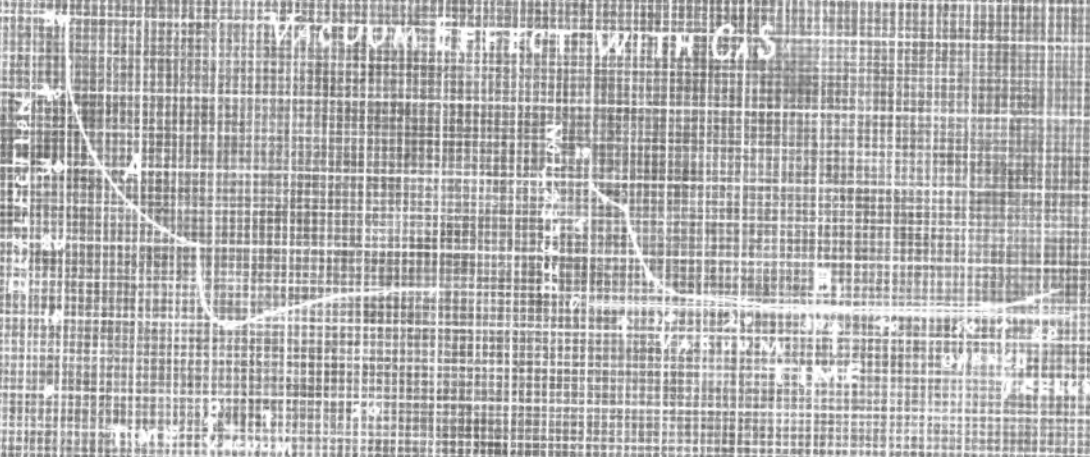


MgO

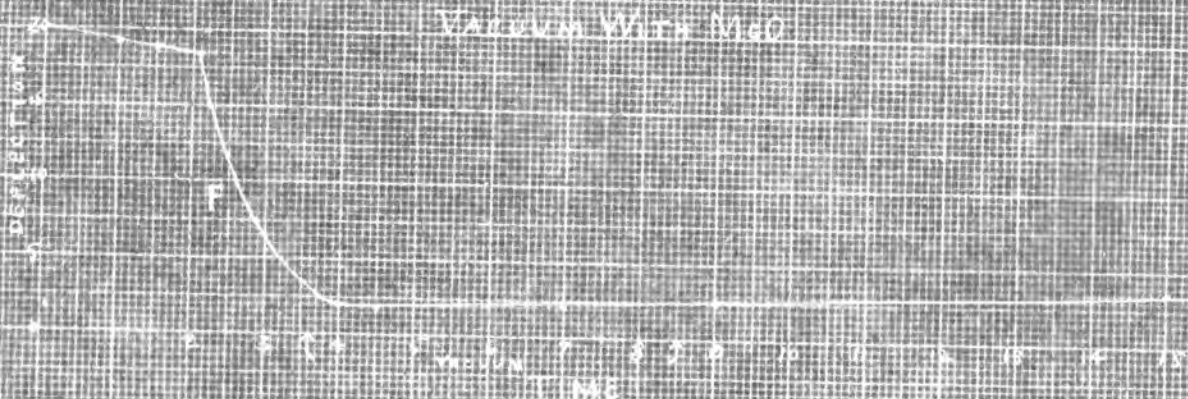




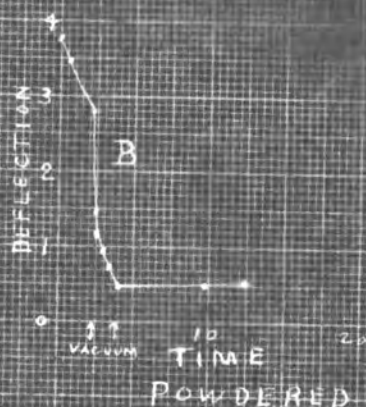
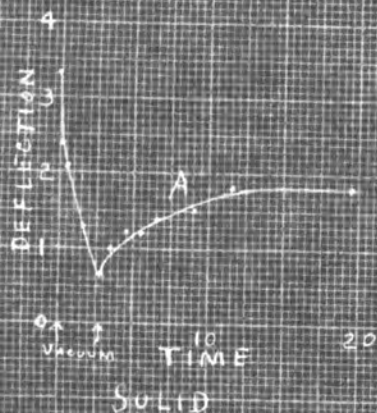
VACUUM EFFECT WITH GAS



VACUUM WITH MHD



VACUUM EFFECT WITH BaS



COOLING EFFECT WITH CaS

