

IV. *Researches on the Electric Properties of Pure Substances.*—No. I. *The Electrical Properties of Pure Sulphur.*

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[PLATES 1–5.]

PRELIMINARY STATEMENT BY PROFESSOR R. THRELFALL.

IN 1886 I began to make some experiments on the specific resistance of certain Australian gums, with a view to finding new insulating material. In connection with this I constructed and tested various galvanometers. In 1887 I was joined by Mr. J. A. POLLOCK, and in 1889 we published conjointly in the ‘Philosophical Magazine’ a paper on the “Specific Resistance of Imperfectly Purified Sulphur,” and on the “CLARK Cell, as a source of Small Constant Currents.” I also published in the same volume a paper “On the Measurements of High Specific Resistances.” All these papers may be considered as preliminary to the present investigation of the behaviour of pure sulphur under electric stress, which has gone on steadily since June, 1889. The remainder of that year, the whole of 1890, and most of 1891, were occupied in preliminary experiments on galvanometers and in making and testing various arrangements of electrodes between which the sulphur to be examined was placed. This work was carried out entirely by Mr. POLLOCK. Early in 1891 I was joined in the work by Mr. J. H. D. BREARLEY, who has worked continuously at the subject with me up to the present time. I began the study of sulphur originally with the object of discovering the exact electrical properties of a pure, non-metallic substance, and chose sulphur because it appeared to offer advantages in melting at a moderate temperature, in being capable of existing in several allotropic forms, and, above all, in being capable of being brought to a high degree of purity with comparatively little trouble. With respect to the galvanometer, which has enabled us to perform the experiments described, so far as its general features are concerned, it was designed by me, in 1890, on the lines laid down in the ‘Philosophical Magazine,’ series 5, vol. 28, p. 473; but the detailed design, as well as the actual construction, I owe

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to Mr. COOK, who made the instrument in the Laboratory workshop. Most of the work in connection with mounting the moving parts and in installing the instrument was done by Mr. BREARLEY.

A great, if not the chief, difficulty, in attempting to form a theory of electro-chemistry lies in the uncertainty surrounding the data. The memorable researches of KOHLRAUSCH on the conductivity of water, as well as those of DIXON on the effect of a small impurity on the mode of combination of gases, together with the quite allied and equally peculiarly large variations produced in thermoelectric power and contact force phenomena by minute differences of chemical composition, have had a most destructive effect on the theories of twenty years ago. It is not too much to say that the electrical action of most bodies in a pure state is entirely unknown at present, although the fact of the continuity of the electrical properties of certain substances—*e.g.* mercury, gold, and copper—as they are more and more purified, raises a hope that the properties of substances as at present investigated may only differ quantitatively from their properties when pure; but whether this be so or not can only be decided by experiment. The question as to the effect of purification is one which must be discussed in each separate case, and probably over and over again, for the word “pure” has no significance except with respect to a definite state of the art of chemistry. It is to be noted that the final stages in a process of purification must always depend more or less upon hypothesis—for a point is soon reached where the impurities become too small in amount to be amenable to ordinary chemical examination. Theoretically this can be got over by operating on large quantities of substances, but in practice such is not found to be the case, for the greater the bulk of substance to be prepared, the more time is required for its preparation\* and the greater is the chance of small and unnoticed accidents occurring. In the case of sulphur this is particularly well marked, for the chief source of impurity is in dust from the air—which leads to a contamination almost proportional to the time required in making the preparations. We look forward to the time when the exclusion of dust during chemical operations of precision will be regarded as of as much importance as its exclusion in bacteriological research. The sulphur we have used is probably as pure as it can be got without taking special precautions to avoid all contact with dusty air. The absence of such precautions vitiates to a great extent many observations of discharge in air, and led QUINCKE† to explain away the diminution of the resistance of benzene and other liquids of small conductivity with increased voltage per unit length.

In the case we have studied, the physical action of dust particles is not to be feared, and appropriate means were adopted for minimising the possible chemical action between dust and sulphur.

One of the results we have attained with sulphur in a certain condition—is a

\* STAS, “Recherches.”

† QUINCKE, “Wied. Ann.,” 1886. vol. 28, p. 546.

similar diminution of resistance, and in this case QUINCKE's explanation is impossible. The suggestion is obvious that the phenomena observed by QUINCKE may possibly be real phenomena—not depending on dust particles—and if this be the case, then it is clear that a valuable discovery has been rendered unavailable by the source of uncertainty we are dealing with.

In the following statement we shall explain with some minuteness the methods adopted for purifying our material, and give a summary of the conclusions to which previous observers have been led as to its physical properties. We shall then explain in a general way the methods we have used for determining the electrical properties. This will be followed by a short treatise on the construction of sensitive galvanometers of high resistance, together with an account of the experiments which have led us to the construction of our instrument, of which full details and drawings will be furnished. We shall then proceed to deal with our various experiments. At the present time the experimental work is still in full progress, and is likely to continue, for in investigating properties of substances the end is only reached when the observer's interest falls off. Our chief reason for publishing is that we consider the main features are now pretty well established.

## SECTION I.

### *On the Preparation and Properties of Pure Sulphur.*

§ 1. *General Discussion of Causes, Procedure, &c.*—Our information on the transformations of sulphur is chiefly derived from the following authors :—

- 1856. C. SAINTE-CLAIRE DEVILLE, 'Ann. de Chim. et de Phys.,' Sér. 3, vol. 47, p. 94.
- 1854. MAGNUS, 'Pogg. Ann.,' 1854, vol. 91, p. 308.
- 1854. B. C. BRODIE, 'Proc. Roy. Soc.,' vol. 7, p. 24 (March 30th, 1854).
- 1856. MITSCHERLICH, 'Jour. für prakt. Chem.,' vol. 67, p. 369.
- 1857. BERTHELOT, 'Ann. de Chim. et de Phys.' (3), vol. 49 (two papers).
- O. PETERSEN, 'Zeitschr. für Phys. Chem.,' vol. 8, p. 608.
- 1884. REICHER, 'Chem. Centr. Blatt,' 1884, p. 450.
- 1889. J. MONCKMAN, 'Proc. Roy. Soc.' for 1889, vol. 46, p. 136.
- 1874. D. GERNEZ, 'C.R.,' vols. 79, p. 219, 82, p. 1151, 83, p. 217.

There are a large number of other observers whose work does not bear so precisely on the subject of the present investigation, and whose names are recorded in the "Sachregister zu den Annalen der Physik und Chemie," published in 1888, p. 563.

Amongst the authors mentioned, we have found the papers of BRODIE and BERTHELOT of most service. BRODIE gives an account of the transformations of sulphur, but unfortunately omits many details, particularly as to the mode of

purification adopted. BERTHELOT attempts to classify the varieties of sulphur on electro-chemical principles. According to him, sulphur exists in two principal modifications, one, electro-positive sulphur, liberated at the positive-electrode during the electrolysis of chloride of sulphur; the other electro-negative sulphur liberated at the negative electrode during the electrolysis of metallic sulphides.

The electro-positive sulphur comprises all those varieties which are amorphous; the electro-negative all those which are crystalline. The distinction between crystalline and amorphous sulphur appears to us to be much more fundamental than between those varieties which are soluble and those which are insoluble in carbon bisulphide. Indeed, as is well known, mere crystallization from carbon bisulphide often involves the formation of insoluble sulphur. The distinction between the main varieties is considerable from the dynamical point of view—for the thermal changes involved in passing from one to the other are very great—as was shown by BRODIE in a simple experiment and by PETERSEN in an elaborate thermo-chemical research.

We have chiefly examined those varieties of sulphur which are sufficiently definite and permanent to enable us to be sure that we are dealing with pure substances. Thus we have examined the monoclinic variety of sulphur pretty thoroughly, together with what we believe we are the first to recognize as a new variety of monoclinic sulphur, as well as several mixtures of this variety with amorphous sulphur obtained by cooling rapidly from a high temperature. The permanence of monoclinic sulphur we find to be much greater than is generally supposed, at least, if the melting point may be taken as a criterion,\* while as for octahedral sulphur, the only possible means at our disposal for obtaining it pure—viz., by the method of GERNEZ—has hitherto failed in our hands. This method is based on the obtaining of sulphur in a state of “surfusion.” The sulphur, which is perfectly crystalline to begin with, is melted below  $130^{\circ}\text{C.}$ , cooled to, say,  $101^{\circ}\text{C.}$ , and then caused to crystallize in the octahedral form by sprinkling the sulphur with a trace of the dust of octahedral crystals. This appears to be a matter of some delicacy, and in the course of a good many trials we have not succeeded to our satisfaction, even when following M. GERNEZ's instructions most minutely. The fact is, that melted sulphur has a very strong tendency to crystallize in the monoclinic form, and this tendency can only be overcome under the most favourable circumstances (if at all) and by the exercise of great care. For most electrical experiments, however, it is necessary to obtain a film of the material between two conducting plates which serve as electrodes, and the conditions attending the production of such films are experimentally unfavourable to forced octahedral crystallization. Again, both FOUSSEREAU (*C.R.* 97, p. 996) and BOLTZMANN, ROMICH and FAJDIGA, and NOWAK (*Sitzungsber. der Wiener Akad.*, vols. 68 and 70) found no appreciable conductivity in crystals of octahedral sulphur, though their methods were not very searching.

\* The phenomena attending the transformation of monoclinic into octahedral sulphur will be dealt with during the discussion of special cases.



## SECTION II.

*The Preparation and Testing of Samples of Sulphur.*

The earliest note we have found on the influence of minute traces of impurity on the properties of sulphur is by MITSCHERLICH in the 'Journal für Praktische Chemie' for 1856, vol. 67, p. 369. This chemist states that the discoloration of sulphur which has been heated to the boiling-point is to be traced to the presence of organic compounds. One three-thousandth part of "grease" will produce a very deep red coloration in sulphur which has been heated to the boiling-point, and even the greasiness produced by handling is said to notably affect the colour of sulphur. The strongly coloured organic compound does not come over when the sulphur is distilled, and its presence may be detected on the bottom of the retort, where it forms black spots. MITSCHERLICH considers the supposed coloured varieties of sulphur discovered by MAGNUS ('Ann. de Chim. et de Phys.,' [3], vol. 47, p. 194) to be merely sulphur contaminated by organic matter; he gives, however, no account of his experiments.

MONCKMAN ('Proc. Roy. Soc.,' 1889, vol. 46, p. 136) noted the black spots which are left in a retort from which sulphur has been distilled, and considers they are produced only when the retort is heated by the bare flame—a process leading, of course, to the heating of the glass much above the boiling-point of the sulphur. BERTHELOT (*loc. cit.*) is inclined to agree with MITSCHERLICH as to the influence of small organic impurities on the colour of sulphur.

STAS ('Recherches.—Bull. de l'Académie Royale de Belgique,' 2ème série, vol. 10, p. 253) made use of the vapour of "pure" sulphur, but gives no details as to how it was obtained. We know of no discussion as to the minute purification of sulphur except the one contained in MONCKMAN'S paper—in which he refers to a method proposed by one of us, and carries out that method and several others in a very careful manner. We must therefore consider the purification of sulphur from the commencement, since there is practically no previous work to help us—we have, in fact, to solve the problem of purifying sulphur and of recognizing it in the state of purity. Our experiments lead to the following result.

Pure sulphur can be recognized chiefly by its negative characteristics. It evaporates from a platinum basin without residue, it has little or no smell, it has a clear yellow colour even when suddenly cooled from above 180° C. by water; it gives off no gas when heated *in vacuo*, it leaves no black spots when distilled from a retort with or without the bare flame; it has a specific resistance of above  $10^{28}$  C.G.S. units when perfectly crystallized in monoclinic prisms; it exhibits, to all intents and purposes, perfect freedom from "electric absorption" when in this state, and it is perfectly soluble in carbon bisulphide, forming a solution which is absolutely clear. We will now give a short account of how these characteristics were determined.

The question of the colour of sulphur occupied one of us previous to 1888, and in that year, and as a result of a good many trials, it was found that when sulphur is

distilled over and over again in glass retorts, black spots always make their appearance in the residue unless the operation is carefully shielded from the action of dusty air. If sulphur is distilled and then exposed to air so that dust can settle on it, then, on repeating the distillation, black spots make their reappearance. We have only once succeeded in absolutely preventing the presence of black spots in a retort from which sulphur was distilled, but we have noted over and over again that just in proportion to the precautions that are taken to exclude dust, so do the black spots become smaller and fewer, and the colour of sulphur suddenly cooled from a high temperature clearer and clearer.

That pure sulphur has no smell we know, because we have prepared a sample by precipitation of hyposulphite, and after five distillations no smell could be detected from it. This observation is important, for we have large quantities of sulphur twice distilled from Sicilian roll sulphur which leaves no residue when burned away in a platinum dish, which remains bright yellow on cooling quickly, which will yield no gas when heated *in vacuo* up to near its boiling-point, and which generally might be considered to be satisfactory had it not the well-known sulphury smell, which, by the way, we consider to be possibly due to traces of chloride of sulphur. The smell is not to be removed by exposure *in vacuo* at any temperature and during many hours, and samples of sulphur which possess it had better be left on one side.

Pure sulphur, of course, leaves no residue on burning in a platinum basin, but we have never succeeded in reaching this stage with sulphur which is burned in the ordinary way. We have, however, got as far as this—that the combustion of 200 grams of sulphur in a platinum dish will leave a stain so small that it cannot be observed unless the platinum is brightly polished. The stain disappears at a red heat, and may be safely attributed to the dust which gets into the dish during the time the sulphur is being introduced, and while the process of burning is being observed. In order to obtain the maximum residue from any sample of sulphur, the last cubic centimetre or so must be boiled off very carefully and without overheating. The residue which, with our purest sulphur, such as we have used in electrical experiments—is after all a mere stain, is far beyond the powers of the balance to detect. It is dark in colour and burns off at a red heat, indicating that it is composed of the same organic compound which was discovered by MITSCHERLICH. We have observed that after a sample of sulphur has been exposed to the air during electrical experiments, it will give a comparatively large residue, although when first prepared the residue could only be observed by close attention. Those samples of sulphur which when suddenly cooled appeared of a buff colour, always gave comparatively large residues, and these were the samples which had been most exposed to the action of air. Of course ordinary sulphur leaves a large quantity of earthy residue besides, which can be got rid of by about two distillations—but we are not discussing such preliminary purifications. Impurities which can be detected by the means above described may be considered to be the more obvious impurities, and do not give rise

to any great concern. Above this point, unhappily, we are obliged to proceed by way of hypothesis, and so conduct the process of purification as to tend to eliminate impurities, which our general knowledge of the chemistry of sulphur leads us to suppose may be present in quantities too small for detection by chemical means. Only those impurities are to be feared which will distil with sulphur, or be mechanically carried over during distillation, and dissolve in carbon bisulphide. This practically narrows the investigation down to the consideration of selenium as an impurity.

In order to cause any residual impurity to vary in different samples, we have tried a large number of different sources for our sulphur. Of these we retain three. The first is by decomposing commercial sodium-thiosulphate by pure hydrochloric acid, washing the deposited sulphur with platinum distilled water, and distilling till the residue on combustion is inappreciable. This method has the advantage of involving no contact with carbon compounds, and of giving rise to no impurities except those that are soluble in water, or left on distillation. As to the impurities which may be suspected to be present in the thiosulphate originally, these will be dealt with when we consider soda waste as a source of sulphur or thiosulphate.

The second kind of sulphur which we have employed is that derived from the polysulphides of calcium. Some roll sulphur, in powder, was digested with marble-lime in the usual manner. The yellow liquor obtained was decomposed by pure hydrochloric acid, and the precipitate washed and distilled.

The third kind of sulphur is some recovered sulphur that came into our hands by the kindness of Mr. F. WRIGHT, of ELLIOTT BROS., importers of drugs in this city. We could get no information at all as to where it came from, or what the process of recovery was; but we were told that the sample (amounting to about 5 lbs.) was recovered and very pure. A very few trials showed us that, as far as the negative characteristics go, the claim of purity was well founded, for the sulphur was at least as good as our precipitated sulphur after about three distillations. To find out where it came from, with a view to investigating its history, we wrote to Mr. J. F. CHANCE (who was known to us as an authority on recovered sulphur) asking him whether he knew of any ordinary process by which sulphur of such a high degree of purity was produced commercially, and whether he could obtain a fresh supply for us. In reply Mr. CHANCE gave us a general account of the method of sulphur recovery invented by himself, and most kindly presented us with a large quantity of sulphur recovered by his process. On comparing this sulphur with that which we had received from Mr. WRIGHT, it became obvious at once that the latter had been produced by the Chance process: the appearance alone is almost unmistakable. According to Mr. CHANCE, the moisture and non-volatile impurities amount together to not more than .01 per cent.—and the non-volatile impurities to perhaps only .001 per cent.—with regard to the latter number we can say that our experience roughly confirms this estimate, for we never obtained a weighable residue even from the evaporation of several ounces of the fused and filtered sulphur. Traces of selenium

and arsenic, however, might occur as volatile impurity, and it was therefore necessary for us to ascertain their presence (or absence) by means of a direct experiment.

After a considerable amount of preliminary work we fell back on the combustion of quantities of about twelve grammes of the sulphur to be tested, in a platinum boat in a combustion tube. The products of combustion being mixed with excess of oxygen and passed over spongy platinum, the resulting sulphur trioxide was received in a large globe cooled by ice and salt. The trioxide was then converted into sulphuric acid, and tested for arsenic and selenium. We made two successful combustions, using in one case the residue from a distillation of Chance sulphur, and in the other the sulphur in the state (twice distilled) in which it was used in our experiments. The combustion requires some precaution. In our arrangements, the tube employed was of hard glass, and was heated for a length of 80 centims., it was 1.4 centim. in internal diameter. In this tube 15 centims. were occupied by the platinum boat containing the sulphur, this was followed by a "mixing" space of red-hot asbestos for 25 centims., and 35 centims. were occupied by spongy platinum and platinized asbestos. Oxygen was admitted by two tubes, one only just entered the combustion tube and provided the oxygen for the burning of the sulphur in the boat; the other ran over the boat and delivered a large excess of oxygen into the "mixing" space. Oxygen was observed to be in excess during the whole process. By regulating the oxygen supply and the temperature of the sulphur in the boat, the combustion can be got to proceed regularly. The combustion tube was bent at the delivery end, and dipped into the receiver. At the close of the operation, a stream of oxygen was passed for some time, the tube being now red-hot throughout—up to the bend—by this means the whole of the contents of the boat were burned and all residues chased out of the combustion tube. Finally the part of the tube which projected into the globe was washed out with platinum-distilled water and the solution added to the solution in the same water of the sulphur trioxide contained in the globe. In the first combustion the oxygen supply was not in sufficient excess during a few moments and the trioxide was coloured blue by combination with a trace of free sulphur. In the second combustion, in which the oxygen was in great excess throughout, the resulting sulphuric acid contained sulphurous acid, and the excess of oxygen also carried off sulphur dioxide during the process. The conclusion seems to be that Sulphur Trioxide is dissociable by spongy platinum at a red heat, even in presence of oxygen—this we did not know, it is not mentioned by LEMOINE ('*Etudes sur les Equilibres Chimiques*'). The solution of trioxide from the first combustion required to be filtered; the second did not, and was absolutely clear and colourless. We remark on this, for there is a chance of selenium separating during the solution of the trioxide, in the presence of sulphurous acid. In both cases the solution was next boiled with a large excess of sulphurous acid and hydrochloric acid. In neither case was there the slightest precipitate. We are satisfied that, under the conditions of the experiments, this means that there could not have been more than

·03 milligram of selenic acid present, or say ·014 milligram of selenium, or about one part in a million. As at first we under estimated the delicacy of the selenium test, it may be worth while to indicate how the test should be performed in order to give the best results. The points are: (1) a large quantity of hydrochloric acid should be used; (2) the liquid after some minutes' boiling should be cooled before the sulphurous acid is added; (3) the mixture should then be well shaken; (4) on heating to boiling, a precipitate will appear in two or three minutes if selenium is present—at the limit a yellowish rose-colour will be produced, but no actual precipitate. The essential point is to have the volume of liquid as small as possible. For instance, with one cubic centimetre of liquid ·01 milligram of selenic acid may be detected with certainty, and still smaller quantities in proportion as the volume of liquid is smaller.

After testing for selenium, and taking the most refined precautions as to re-agents, the MARSH'S test for arsenic was applied. In no case was arsenic discovered. We found by direct experiment that the minimum amount of arsenious oxide we could detect by our appliances was ·02 milligram, and that by the smell of the gas only. The test, however, as made by the nose is just as certain as that made by the eye when a mirror is produced; the latter, however, is less delicate. With respect to precautions, we will only say that the instructions of FRESSENIUS were carefully followed, and that this was not the first occasion on which we had made the test.\*

We may conclude that if arsenic is present in the sulphur, it is only so to an extent of about one part in a million. The selenium test will be observed to be more delicate than the arsenic test—a fact not generally recognized—and this when the test is made by noting the smell of the evolved hydrogen. If a recognizable mirror be required, the arsenic test is a good deal less delicate.

A test for tellurium and selenium was made for one of us in 1888 by Dr. HELMS, on a sample of sulphur recovered from thiosulphate. These results were negative.

As regards arsenic and selenium, we wish to go further, and to show that it is very improbable that they could have been present even in quantities much less than we could have detected. The results of the enquiry will apply alike to sulphur recovered by the Chance process and to sulphur recovered in the laboratory from commercial sodium thiosulphate (assuming the latter to have come from soda waste). For this purpose it is necessary to consider the LEBLANC process in some detail.

The sulphuric acid employed in the salt-cake process is the source from which arsenic and possibly selenium may be derived. The greater part of the arsenic is got rid of in the salt-cake furnace in the form of chlorides. With respect to selenium, we believe that it will be almost all precipitated in the sulphuric acid chamber, but as the acid is not filtered, as a rule, this cannot be regarded as a purification.

\* We may note here that the decomposition of arsine by strong sulphuric acid is a test which, though not quite so delicate as the mirror test, is not by any means a bad one. It is not usually given as a test at all. (The sulphuric acid must be kept concentrated.)

Dr. GEORGE ELLIOTT informs us that when burning some samples of sulphur from Japan, containing about 1 per cent. of selenium, for the purpose of making sulphuric acid, the selenium separated in the denitrating tower and in the chamber, in the manner we suggest.\* In order to find whether selenium is got rid of in the salt-cake process, we burned a quantity of selenium in a properly bent tube, and passed all the products of combustion into water, burning the selenium part of the time in a brisk current of oxygen, and part of the time with only just enough oxygen to keep the selenium alight. Part of the resulting selenious acid was converted into selenic acid, and a mixture of these acids and selenium, together with any other of the products of combustion of selenium which might have been formed, were added to some sulphuric acid in an experiment imitating the salt-cake process. We found that all the selenium remaining in the salt-cake did not amount to 1 per cent. of that mixed with the sulphuric acid at the commencement of the process, so that the salt-cake process gets rid of most of the selenium as well as the arsenic.

It is possible for some small trace of selenium to get into the black-ash furnace. If it does, it is presumably in the condition of free selenium, sodium selenate, or selenite. Now the trace of free selenium will probably be volatilized to a great extent, and pass off with the other gaseous products. As for the selenite and selenate an experiment to be described indicates that they will be decomposed, yielding free selenium, with which some of the lime will form calcium selenide. We find, however, calcium selenide is decomposed when suspended in water by carbonic acid gas yielding free selenium, but not a trace of selenium hydride. These facts were established as follows:—

About 4 grams of precipitated chalk were converted into calcium selenate, and this was reduced by hydrogen (pure) to calcium selenide. During the operation much of the selenide decomposed into free selenium and lime (?), and there was a considerable evolution of selenium hydride. The process was stopped while the evolution was in full progress. On washing the contents out of the tube we probably had a mixture of free selenium, calcium selenide, calcium selenate, and perhaps other products. A stream of carbon dioxide gas (pure) was passed through this mixture, including the water, contained in a set of potash bulbs, and as a result a large quantity of selenium was deposited, but not the slightest trace of selenium hydride could be discovered either by the smell of the emergent gas or by heating the delivery tube red-hot.

It will be noticed that the great instability of calcium selenide (for we presume that the hydrogen selenide came from the reduction of this salt), when heated to redness, gives us another reason for suspecting that very little calcium selenide is formed in the black-ash furnace—or rather that very little can survive, unless reduction

\* A subsequent note from Dr. ELLIOTT throws some doubt on this, for a red precipitate being noticed at the foot of the denitrating tower—when sulphur nearly, if not quite, free from selenium was being burned as a source of sulphur dioxide—an analysis of the precipitate was made. It then turned out to be ferric oxide.

by carbon and carbon gases differs very unexpectedly from reduction by hydrogen. Any alkaline selenide that might be formed is unimportant, because, firstly, it would be soluble in water, and, secondly, it is not stable in solution but deposits selenium, forming, perhaps, some oxyacid of selenium. If this be the case, carbonic acid gas might liberate an oxide of selenium, but this would not volatilize at ordinary temperatures. It is possible, finally, that free selenium in the waste might gradually combine with the excess of lime, if there be an excess, and re-form selenide of calcium. This was tried by boiling finely powdered selenium with excess of lime—but no combination was produced during an hour, and operating on about half a gram of selenium.

The case for the probable absence of selenium from Chance sulphur seems therefore to be pretty well made out, as well as for its absence from commercial thiosulphate of sodium.

#### *Other Methods of Purification.*

We have purposely omitted to use any method based on the crystallization of sulphur from organic liquids or sulphur dichloride. Our reasons are very simple—anyone who has crystallized sulphur from carbon disulphide must have noticed that on reducing such crystals to powder, even long after they have appeared perfectly dry, a strong and horrible smell, characterized by all the worst features of the odour of impure carbon bisulphide, becomes immediately perceptible. Since powdering the crystals reduces them only to smaller crystalline fragments, there is no reason why volatile compounds should not continue to linger in them. If this be the case, what are we to expect on distilling? Surely it is gratuitous to assume that organic compounds could not be formed and distil with the sulphur. Supposing these compounds to be without smell, how could they be detected? Again, carbon bisulphide is a liquid almost impossible to purify, it begins to decompose immediately under the action of light, and forms unknown compounds. Judging by the smell still clinging to some carbon disulphide very carefully prepared by one of us, we may hazard a guess that some selenium compound still lingered. As to toluene, turpentine, &c., considered as solvents of sulphur, we have never seriously entertained the idea of using any of them, for fear of introducing volatile carbon compounds—and also because we have an idea that, owing to the comparatively small solubility of sulphur in these substances and the necessarily large amount of the solvent, traces of impurity might possibly accumulate in the sulphur. It surprises us that anyone conversant with, say, the curiously complex contents of rock crystals, should rely on crystallization to remove impurity.

Worst of all possible solvents, in our opinion, is chloride of sulphur. Chlorine is most difficult to purify, and the process of preparation of chloride of sulphur involves uncertainties to which exception may be taken. Even supposing this solvent to be

obtained in a pure state, there is no more difficult substance to remove from the sulphur\* (compare MONCKMAN, *loc. cit.*). It is altogether a most unsatisfactory body to deal with.

*The Gaseous Contents of Sulphur.*—On heating sulphur *in vacuo*, there is no doubt that gases are given off, even from the purest samples. The following is an account of some experiments made on this subject in connection with what will later on be described as the “Film of November 18th, 1892.” It may be premised that this was a film which had been rapidly cooled from a high temperature, after having been part of some sulphur which had caught fire in an atmosphere containing much carbonic acid gas, and which looked rather dirty. The sulphur composing this film was found to give off a good deal of gas on heating; so, on November 22nd, 1892, a quantity of recovered sulphur, twice distilled, was selected for an experiment having for its object the determination of the conditions under which gas is given off and absorbed by sulphur. The sulphur was melted under an air-pressure of about 5 centims. of mercury; the results were—

Hardly any gas was given off till the thermometer rose to 178° C., and then the evolution of gas increased up to 190° C. At this point the increased viscosity of the sulphur prevented the bubbles coming off, but they were still being formed. At about 230° C. the bubbles began to separate from the sulphur, and continued to do so up to the boiling-point. There was nothing like a sudden evolution of gas at any temperature. The next day the sulphur was re-heated to 240° C. under similar conditions, but not a single bubble of gas could be detected.

A question now arose as to the nature of the gas. Is it air? If so, shaking up the sulphur with air while it cools from the boiling-point might be considered to be likely to induce more air to get absorbed. This was tried, but no bubbles were given off on re-heating under an air-pressure of 5 centims. of mercury only. Is the gas carbon dioxide? The last experiment was repeated in an atmosphere of carbon dioxide, but again no gas was driven off on re-heating. Has the gas anything to do with the sulphur being on fire?—*i.e.*, is the gas an oxide of sulphur dissolved from an atmosphere mainly composed of this oxide? To test this, the sulphur was heated to boiling-point and set on fire in a platinum dish, a bell jar was placed over it, and the sulphur was agitated freely. It was then re-transferred to the vacuum-bath and tested as before, but little or no gas came off.

These experiments give no clue as to what the gas given off really is, but a valuable result is that, when once the gas has been caused to come off, remelting will not cause more gas to be absorbed. In view of the more important questions awaiting solution, we judged it unadvisable to spend any time in further determining the nature of the gas, as we possibly might have done in a vacuum-tube by the help of spectroscopy. We conclude, however, that the purest distilled sulphur ought to be

\* 1893.—It can be done however by continued extraction with carbon bisulphide—at all events fairly well (see end of paper).



remelted *in vacuo* before being used—but this we only began to do in 1893, after the above facts were discovered. We should like to hazard the mere guess that the gas is water vapour, and that it is taken up during the formation of the sulphur snow, which is always present when sulphur vapour condenses in a retort and receiver.

*General Physical Properties of Purified Sulphur.*

We have not any very serious corrections to make to the observations of previous workers—in other words, very pure sulphur does not differ appreciably in ordinary characteristics from sulphur which is only moderately pure. The most obvious physical datum of a fusible solid is the melting-point, and this is, in the case of sulphur, still rather a matter of uncertainty. The most important contribution to our knowledge of this constant was supplied by B. C. BRODIE ('Proc. Roy. Soc.,' vol. 7, p. 24) in the year 1854. The main results, as far as melting-point is concerned, are as follows :—

1. Pure (?) octahedral sulphur crystallized from carbon bisulphide melts at  $114^{\circ}\cdot5$  C.

2. But octahedral sulphur begins to change into monoclinic sulphur below this temperature ; and

3. The melting-point of pure monoclinic sulphur is  $120^{\circ}$  C.

4. Mixtures of octahedral and monoclinic sulphur melt at temperatures between  $114^{\circ}\cdot5$  and  $120^{\circ}$  C.

No data are given as to how the sulphur was purified, nor as to the method adopted for finding the melting-point. We will add to this statement the following account, which may be regarded as summarising a large number of experiments.

*Method.*—We have always employed the method of heating small particles in thin glass tubes alongside a thermometer. We are aware (though we cannot find the reference) that a recent observer who carefully examined the relative accuracy of different methods, decided that the best method to employ in determining melting-points is that of using a large quantity of the substance and plotting a cooling curve. In the case of sulphur, however, this method is rather difficult for many reasons—some of which will be evident on referring to BRODIE's paper—and with any method the very small conductivity of sulphur constitutes a grave difficulty.

Our thermometers, which we had hoped to have standardized at Kew, were, by an oversight, only standardized up to  $100^{\circ}$  C., and to send them to Kew for the oversight to be remedied would have required too much time. They were, however, very good. One was six years old at least, and its B.P. was too high by  $1^{\circ}\cdot34$  C. We have confidence that the observations are correct, as far as the thermometers go, within about  $\cdot1^{\circ}$  C., within which limit the thermometers were in accordance at the temperatures dealt with, the boiling-point corrections being made.

*Octahedral Sulphur.*—The observations were as follow for octahedral sulphur crystallized (and well dried) from carbon bisulphide :—

Sulphur heated in a glycerine bath at rate of about  $5^{\circ}$  per minute.

TABLE I.—Melting-point of Octahedral Sulphur.

Number of experiment.	Sulphur began to melt at	Sulphur completely melted at
	$^{\circ}\text{C.}$	$^{\circ}\text{C.}$
1	114.4	116.86
2	119.86	120.86
3	116.06	116.06
4	118.46	120.66
Mean . .	117.19	118.61

As BRODIE has shown, octahedral sulphur heated beyond about  $100^{\circ}\text{C.}$  begins to turn into monoclinic sulphur. If the sulphur is in the state of fine powder, the change cannot be avoided even if the sulphur be heated “for the shortest time between  $100^{\circ}$  and  $114^{\circ}5\text{C.}$ ” As our sulphur was in small fragments, it was possible that the above discrepancies could be attributed to a more or less partial change having occurred. In order to test this, the glycerine bath was brought up to different temperatures near the melting-point before the sulphur was introduced. The results are as follow :—

TABLE II.—Melting-point of pure Octahedral Sulphur.

Number of experiment.	Initial temperature of bath.	Sulphur began to melt at	Sulphur entirely melted at	Remarks.
	$^{\circ}\text{C.}$	$^{\circ}\text{C.}$	$^{\circ}\text{C.}$	
5	116	116	116	Went at once Ditto
6	115.86	115.86	115.86	
7	115.06	115.86	115.86	
8	108	115.46	116	
9	106	115.06	116.06	
Mean (reject- ing No. 8) }	..	115.69	116.00	

These observations were made by Miss FLORENCE MARTIN, a most careful observer, to whom our thanks are due. She recommends that Experiment No. 8 should be discarded, on the ground of the point of commencement not having been so sharply marked.

It will be noticed that the above tables indicate two things : firstly, that on the whole the melting-point is lower when the sulphur is raised to it suddenly ; and secondly, that all the melting-points are considerably above those given by BRODIE. The reason probably is to be found either in the fact that BRODIE used imperfectly

purified sulphur, or that there is a constant error in our thermometers, which we have no reason to believe. The fact probably is that BRODIE did not sufficiently purify his crystals from the evil-smelling compounds which they carry with them from the bisulphide.

*Monoclinic Sulphur.*—The melting-point of perfectly soluble monoclinic sulphur was taken by the same observer in connection with a film which had been experimented upon.

TABLE III.—Melting-point of Aged Monoclinic Sulphur.\*

Number of experiment.	Sulphur began to melt at	Melting complete.
1	° C. 119·46	° C. 119·96
2	120·06	120·46
3	119·06	119·96
Mean . .	119·53	120·13

This agrees as well as can be expected with the observations of other observers on monoclinic sulphur. The fact that the melting-point of monoclinic sulphur, even when it has lost its crystallographic properties, is about 120°, may be taken as established by these observations. The want of sharpness in melting-point, which is to be noticed even in the case of monoclinic sulphur, is marked in all the samples we have examined, and is on the whole more pronounced when we deal with mixtures, but not markedly so. We think it is established that sulphur, like selenium, has not a perfectly sharp melting-point—another point of resemblance between these substances which we have not seen noticed. Of course, the effect is much more marked in the case of selenium than in the case of sulphur; but even with the latter the corners of fragments become less sharp and assume a greasy appearance at temperatures a good deal below those at which the fragment is definitely liquid.

The freezing points of sulphur have not been investigated by us, as they have been dealt with most elaborately by GERNEZ ('C.R.,' *loc. cit.*). One disadvantage of the method of publication adopted in those famous "Comptes" is that it effectually prevents any estimate being formed of the reliability of experimental work, the scarcity of space not allowing sufficient details to be given.

The melting points of mixtures of monoclinic and electro-positive sulphur are

\* This sulphur was afterwards found by Professor DAVID to have lost its crystallo-optic properties, and could not be distinguished by the polariscope from octahedral sulphur. We have ventured to call this variety "aged monoclinic" sulphur. It is probably generally formed as a preliminary step in the formation of octahedral sulphur from monoclinic at ordinary temperatures.

rather below  $120^{\circ}\text{C.}$ , and will be dealt with when the films forming the subject of experiment are considered. The detail of some other physical properties will be dealt with as occasion arises.

### SECTION III.

#### *Methods of Determining the Electrical Constants of Pure Sulphur.*

The chief constants determined by us are the Specific Resistance and Specific Inductive Capacity. Observations have also been made on the residual charge of sulphur regarded as a dielectric. No observations on the conduction of electricity through liquid sulphur have as yet been made, this having been provisionally accomplished by previous workers. On the other hand, the phenomena attending conduction through solid sulphur have been made out by us, at least, in their more important features.

It will be convenient here to give a sketch of the information obtained by previous observers.

#### *Resistance of Sulphur.*

WIEDEMANN, 'Lehrbuch,' vol. 1, p. 498. Sulphur is mentioned as a non-conductor.

BOLTZMANN, 'Wien. Sitzb.,' vol. 70, p. 342. In this paper, which deals more particularly with dielectric constants, it is stated incidentally that sulphur is a perfect insulator, and is free from "dielectrische Nachwirkung."

G. FOUSSEREAU, 'C.R.,' vol. 95, 1882. This paper contains an account of a method of determining high specific resistances, together with results as to the resistance of glass, which do not concern us. The method employed is that of placing the substance to be examined between two cylindrical electrodes. These electrodes are in series with a battery and condenser, the latter having its armatures connected to the poles of a LIPPMANN electrometer. The observation consisted in noting the time required for the electrometer to register a known difference of potential. From this, and the voltage acting on the resistance cell, and the capacity of the condenser, the specific resistance can be calculated. In 'C.R.,' vol. 97, p. 996, 1883, this method is applied to liquid sulphur, the electrodes being concentric zinc cylinders. We did not believe in the freedom of zinc from action on sulphur, but after a good many experiments on bright plates, in no case observing any effect even up to the boiling-point, we must admit that zinc is probably a safe material to use. No details are given by FOUSSEREAU as to the methods (if any) used to purify the sulphur. The method adopted for examining the conductivity is free from error so far as the action of the containing vessel goes, but not with respect to the surface conductivity. The sulphur experimented upon is stated as having existed in various states which are named, but the paper is not sufficiently detailed to admit of any judgment being formed as to whether these states were actually attained. The results are in brief:—

Specific resistance of prismatic sulphur at  $112^{\circ}1$  C.  $= 7.39 \times 10^{13}$  ohms.

Specific resistance of prismatic sulphur at  $69^{\circ}$  C.  $= 3.93 \times 10^{15}$  ohms.

Below  $69^{\circ}$  C., the conductivity ceases to be measurable. With regard to the observation at  $69^{\circ}$  C., we show that this is not the value for pure sulphur perfectly prismatic. With respect to the value at  $112^{\circ}1$  C., all depends on whether the sulphur is heating or cooling; but, in any case, we consider it is probably too low. It is further stated that the same prismatic sulphur left to itself at ordinary temperatures, devitrifies and assumes an appreciable conductivity. Thus:—

After one day, specific resistance at  $17^{\circ}$  C.  $= 1.170 \times 10^{15}$  ohms.

After two days, specific resistance at  $17^{\circ}$  C.  $= 7.05 \times 10^{14}$  ohms.

This is contrary to our results. Our impression is that probably the sulphur was a mixture of monoclinic and insoluble sulphur, that surface effects were not sufficiently guarded against, and that the sulphur was probably impure. But here again the brevity of the account disarms criticism; we can only say that the results do not agree with ours in any way. There are other remarks on the conductivity of octahedral sulphur, which is said to be zero, and on the conductivity of sulphur in the liquid state, which we have not yet investigated.

E. DUTER, 'C.R.,' vol. 106, p. 836. Some experiments with an induction coil on melted sulphur. The author found traces of action both on gold and platinum electrodes.

J. MONCKMAN, 'Proc. Roy. Soc.,' 1889, vol. 46, p. 136. The most complete record of the electrical properties of sulphur hitherto published. He used a voltage of about 60 volts, and a high resistance galvanometer. The electrodes were of gold or carbon, and the paper is more concerned in establishing qualitative properties than absolute quantitative results. The results are more valuable than any of those hitherto mentioned, because the purification of the sulphur is more fully dealt with. All the numerical results refer to melted sulphur, and therefore will not be dealt with here. The most novel observation is that the resistance of "soluble" sulphur depends on the light falling upon it, a result which is inconsistent with that of a number of experiments, designed to test the point by one of the authors, with the assistance of Mr. J. B. ALLEN.

### *Specific Inductive Capacity of Sulphur.*

An exhaustive list of results up to 1883 is given by GORDON ("Electricity and Magnetism," vol. 1, p. 134 (Table)). The lowest results are those of FARADAY and GORDON, viz., 2.24 and 2.58; and the highest recorded values are those of BOLTZMANN, from 3.84 to 4.773, along a particular axis in octahedral sulphur. Values given by WÜLLNER and BOLTZMANN (by condenser method) lie between the above limits. It is clear that the value of the specific inductive capacity of sulphur requires further

investigation, if only from the great discrepancies which appear above. Other values which have been obtained for the dielectric constant of sulphur will be found in WIEDEMANN'S 'Lehrbuch,' vol. 2, p. 25, and onwards. The only determination of the constant for sulphur in a special state is that of BOLTZMANN, but the purity of the natural crystal he used was not established.

*Methods of Determining High Specific Resistances.*

(1.) The most direct method is that by means of a galvanometer. This method was used by one of us in 1888 ('Phil. Mag.,' 1889, vol. 28). The advantages of the method (which will be fully discussed presently) are that it involves a direct determination of voltage and current, and can be made practically independent of any leakage other than the one under investigation. It is also fairly rapid and very flexible. Its drawback is that large voltages are required, and, as generally practised, the method is wanting in sensibility on the one hand, and is more or less dependent on some assumed galvanometric formula on the other. These difficulties we have, however, overcome. The galvanometric method was used with success by the Brothers GRAY, 'Proc. Roy. Soc.,' 1884, vol. 36, p. 287; MONCKMAN, *loc. cit.*; BROOKS, 'Journ. Soc. Tel. Eng.,' vol. 9, p. 5 (1881); AYRTON and PERRY, 'Proc. Roy. Soc.,' vol. 27, p. 219, 1878, and many others.

(2.) *Leakage Methods.*—These are of two classes, and are so well dealt with in Professor GRAY'S book on 'Electric Measurements' that very little remains to be said here, and that little is only by way of criticism. In the first place, the advantage of the method is that it is very sensitive and convenient, and can be carried out without special training by anyone possessing a good electrometer. Also, it works well over a large range of voltages. The disadvantages for very high resistances are—(1) the insulation of the instrument is only made sufficient with great difficulty, (2) the time required for an observation is very long, and this is apt to mask very important effects. Again, if the calculation of the results be made from the rate of fall of potential with time (as was done by J. J. THOMSON and NEWALL, 'Proc. Roy. Soc.,' vol. 42, p. 410, 1887), a certain want of sensitiveness is to be observed. If, on the other hand, two potentials and two times sufficiently far apart for accuracy are observed, an assumption of a law of resistance (generally OHM'S) requires to be made in order to integrate the equation (GRAY, 'Absolute Measurements,' &c., p. 404), since, in the case of a very high resistance, the fall of potential is a small fraction of the total voltage only. This assumption, although philosophically repugnant, probably does not produce any very disastrous effects on the subsequent statement of results. An objection of greater gravity lies in the fact that very often the capacity of the quadrants of the electrometer cannot be neglected, and as these are affected by electric absorption (with electrometers constructed with glass insulation), a source of uncertainty is introduced. If the potential-time-curve-slope be used to give a value of the equiva-

lent resistance for a definite potential, when neither the capacity of the quadrants nor the leakage of the electrometer can be neglected, then the formula of calculation becomes arithmetically very objectionable. This is by no means a slight disadvantage if many results have to be reduced. The capacity of the resistance cell also has to be known with fair accuracy, which, at all events, involves more work. The gravest disadvantage, in our experience, lies in the variability of the rate of leakage of the quadrants. If the experiment last for an hour, as is often necessary, then undiscoverable changes may have been taking place in the insulation resistances of the electrometer. If a large condenser be employed in order to reduce the magnitude of the uncertainties arising from want of accurate knowledge of the other capacities involved, we have to face the difficulty of making a proper allowance for its probably very variable insulation resistance. With our high resistances this difficulty proved insuperable. Taking everything into account, we do not consider this method favourable for the determination of absolute resistances, particularly when the word resistance has no meaning except with respect to an instantaneous voltage.

In the second class of experiments by the leakage method, the charge which leaks is taken up by an auxiliary condenser. This method has been used by BOUTY ('C. R.,' vol. 110, p. 1362) with fair success, on standard condensers, for the purpose of investigating the phenomena of residual charge. For this purpose, and when the capacities of the different parts of the apparatus are known, the method is suitable; but, as a method for measuring absolute resistances, it merely adds to the uncertainties mentioned above—those due to the uncertainty of capacity and insulation of the receiving condenser. In our case these methods were out of the question, as we had to deal with resistances greater than the insulation resistance of our mica condensers. In the application of this method made by FOUSSEREAU ('C. R.,' vol. 95, p. 216) matters were complicated by the use of a LIPPMANN electrometer, the poles of which can surely only insulate fairly well for small voltages, and which presumably has a not necessarily vanishing equivalent capacity. However, we have not had much experience with the LIPPMANN instrument, so our criticism must not be taken for more than it is worth.

A quite different method has been employed by H. KOLLER ('Sitzungsber. Wien. Akad.,' vol. 98, p. 201). This method consists in placing the substance undergoing investigation, in series with a high resistance constructed either of a tube of sulphate of zinc solution, with zinc electrodes, or of a quantity of saturated solution of iodine in carbon bisulphide with platinum electrodes. The latter resistances may be constructed (with proper precautions) as high as  $10^{11}$  SIEMENS' units. A divided circuit is used to give any desired voltage to the circuit containing the artificial resistance in series with the resistance to be measured. The fall of potential between one terminal of the cell or derivation circuit and the resistance cell, and between the same terminal and the artificial resistance, allow (proper connections being made) of a comparison of the resistance in question with that of the artificial resistance. KOLLER was looking

for qualitative rather than absolute quantitative results, and for this purpose his method has advantages in its quickness and simplicity. If absolute values are required, the method has many drawbacks. The artificial resistances are subject to considerable variation, and are themselves calibrated one from another in such a manner as to give every opportunity for the accumulation of errors. There is reason to suppose that the resistance to feeble currents, such as would be produced by a few cells, will depend on the previous history, and will not be by any means the same when the current is reversed. In KOLLER'S experiments the current was, in general, not reversed; in fact, the peculiar behaviour of the liquids investigated did not permit of the method of reversal being employed in all cases. Since the resistance comparison depends on the comparison of two potential differences, it is necessary to eliminate the electrode effects without taking advantage of the method of reversals. KOLLER allowed for the electrode effects by observing them when no current was flowing, which was, perhaps, as much as the circumstances permitted, but could hardly be considered sufficient when absolute measurements are in question. KOLLER does not appear to have reversed his electrometer (*loc. cit.*, p. 204) in taking his readings; an oversight which, we are persuaded, must damage the authority of his work. We are, however, more concerned to explain why KOLLER'S apparently simple and advantageous method was not suitable for the ends we had in view, than to criticise his work. We may add that the power of the method is finally limited by the want of insulation of the electrometer, but it remains probably the most sensitive method known for the examination of high resistances.

*Method Adopted for Measuring High Specific Resistances and Specific Inductive Capacity.*

The method employed by us\* is substantially the same as that explained by one of us and J. A. POLLOCK, in a paper in the 'Philosophical Magazine,' vol. 28, 1889, p. 469. The sulphur forms a film between two aluminium plates. A voltage up to about 300 volts is supplied by a set of small test-tube accumulators. The sulphur, storage cells, and galvanometer, are placed in series, keys being provided for cutting the galvanometer out of the circuit, and for reversing the current through the galvanometer without reversing it in the rest of the circuit. Readings are always taken by the method of reversing the current through the galvanometer, and observing the first elongation of the needle. Two galvanometers are always in commission—one at a very high grade of sensitiveness known as the "new galvanometer" and the other at a lower grade, read by a spot of light on a scale, known as the "old galvanometer." In order to evaluate the readings of the galvanometers, a second set of apparatus is prepared, consisting of a standard Clark cell, a megohm, and various resistance boxes, whereby any voltage, from that of the cell down to one hundred-

\* See Plates 2-5.



thousandth of the same, may be included in the galvanometer circuit in series with a megohm. A reversing key for the galvanometer and for the cell is provided. The resistances are adjusted till the first deflection of the galvanometer needle on reversal is, as nearly as may be, the same as the deflection when the sulphur is in circuit. The keys are arranged in such a way that the change from the sulphur circuit to the megohm circuit can be made almost instantaneously. In this way a direct value can be assigned to the current causing any deflection of the galvanometer needle, without relying on any particular galvanometer law; both circuits are practically inductionless. It remains to measure the voltage of the storage cells. In our earlier experiments the cells were permanently arranged so as to be tested in sections against a set of 50 Clark cells, or a smaller number by the method of differences employed by Lord RAYLEIGH in his experiments on the absolute electromotive force of the Clark cell ('Phil. Trans.,' 1885). The resistance of sulphur, however, depends so much on previous history, voltage, &c., that a refinement of this kind was soon seen to be unnecessary, and in all the later experiments the voltage was obtained simply by placing the cells in series with a megohm and low resistance galvanometer, and observing the double steady deflection. This was compared with the double steady deflection produced by the 100 volts of the electric light circuit, derived from 31 plate E.P.S. accumulators, and measured by a FLEMING and GIMINGHAM voltmeter, which had been calibrated against Clark cells, but which was found to require no correction at or near 100 volts. The proportionality of the readings of this galvanometer to the currents passing, within the limits employed, was established by a special series of experiments. The galvanometer was a low resistance reflecting galvanometer, very strongly controlled, and was read with a lamp and scale.

It very soon became obvious—especially when the sulphur was heated—that some check must be devised, capable of detecting any breaking away of the film from the electrodes, owing to unequal expansion, &c. An arrangement of resistances for comparing capacities by DE SAUTY's method (see GLAZEBROOK, 'B.A. Reports,' Leeds, 1890, p. 102, or 'Electrician,' October 3, 1890) was accordingly set up in a permanent manner, and provided with keys, &c., so that the capacity of the sulphur cell could be obtained within a few minutes of the determination of its resistance. A certain .2 microfarad division of a condenser by ELLIOTT BROS. was used as the standard, and this was afterwards compared with a condenser by MUIRHEAD, whose corrections were obtained and furnished by Dr. A. MUIRHEAD. The method used by Dr. MUIRHEAD is described by GLAZEBROOK (*loc. cit.*). The uncertainties still remaining in the value of the condenser capacity are probably much too small to require further discussion for the following reasons: When we used the capacity test merely to check the adherence of the film, the absolute value of the standard did not matter, and when we used it to determine the capacity with a view to obtaining the specific inductive capacity of the sulphur, the small thickness of the film (about .25 millim.) prevented its actual thickness being measured with sufficient accuracy to make it worth while to endeavour to go behind Dr. MUIRHEAD's corrections. It is of course, easy to

criticise the DE SAUTY method of comparing capacities as applied to two condensers, one showing absorption and the other not (for sulphur is almost free from this phenomenon), but the largeness of our available voltage and the extreme perfection of our galvanometer permitted us to experiment under very advantageous conditions. For instance, with 100,000 ohms out in one branch, and about 7000 in the other, an appreciable kick was produced when the balance was upset by 1 ohm. Of course, it is necessary to use a thin film of sulphur in order to examine the resistance, and this is not the most satisfactory arrangement for arriving at the best value of the specific inductive capacity. There are two incidental advantages, however, which are of importance in practice. The first is that the correction for the effect of the edges of the plates is small. Thus, the actual area of the opposing plates was in one case found to be 156.445 square centims.; and with a film thickness of .0241886 centim., the correction for the edges (the plates being nearly square) amounted to .26 square centim. only, or about .14 per cent. As it was impossible to insure the plates being *exactly* over one another, and as any deviation from exactitude would diminish the capacity, and as, moreover, it was difficult to avoid the presence of small bubbles (whose area was approximately allowed for), it will be understood that the correction for the edges may be in general left on one side. It was, however, usually applied. Again, the capacity being tolerably large—between  $2 \times 10^{-20}$  and  $3 \times 10^{-20}$  C.G.S. electro-magnetic unit—the capacity of the connections and keys could also be neglected without prejudicing the results; they were, however, included. The disturbance produced in this case will be understood by the statement that the capacity of the keys and leads was measured by the ballistic method, as well as by the DE SAUTY method. The throw was 7.8 divisions for a voltage which gave with the sulphur condenser in as well, 388 divisions. This corresponded to a capacity for the sulphur of .00226 microfarad. Consequently the capacity of the leads and keys, &c., was about 2 per cent. of the capacity of the sulphur condenser. Now we shall show that the specific inductive capacity of prismatic sulphur is about 3.7, and of the same sulphur when mixed with about .35 per cent. of insoluble sulphur is as much as 5.64 in one set of observations.\* Now, whether our results are right or wrong, this shows that the correction of 2 per cent. is not of great importance. It can, however, be supplied if desired, as the key, leads, &c., remained the same throughout, and is supplied with the other corrections in the tables.

The reader may possibly and naturally think that we ought to have observed the specific inductive capacity of sulphur in thick plates in order to get over the uncertainties mentioned, but it was one of our principal objects to discuss the specific inductive capacity as related to the conduction phenomena, and this could only be done with security by making both sets of observations on the same film. That this was a necessity, will be understood after an examination of the tables, which show

\* October, 1893.—We believe this high value is due to some error which, however, we cannot trace. The values of K are elaborately dealt with by the method of weighing later on.

that an admixture of less than 1 per cent. of insoluble sulphur with monoclinic sulphur reduces the specific resistance of the latter (in one case) to at least the millionth part. There is still room, however, for a careful study of the specific inductive capacity of sulphur in its several allotropic states, and with varying duration of charge, in order to discover whether the great differences between the values obtained can be accounted for by what KOLLER calls the "Schliessungs Strom," for, from our experiments, residual effect exists only to a very small extent, even in tolerably conducting mixtures of soluble and insoluble sulphur. This is one of the matters which requires further investigation and is dealt with later.

The drawings which accompany this paper will show the exact arrangements of the experiments, as well as the dimensions of the various parts of the apparatus, for the drawings are to scale with the exception of the resistance boxes in the ground plan. We will now mention one or two points in which we have found it requisite to exercise particular caution; the first of these is the insulation of the apparatus. We have found that if the apparatus is to be left in position for any great length of time there appears to be a distinct gain in making use of a combination of different insulating substances. Thus the "old galvanometer," which is very well insulated itself, stands on three bits of ebonite placed on a clean sheet of glass. This sheet of glass is supported by three combined flint-glass and paraffin insulators, made by placing a small cylinder of paraffin on the top of a flint-glass bottle, and inverting over it a cylindrical glass dish. The outer dish serves to protect the paraffin against dust; the whole stands on a large slab of ebonite 1 inch thick. All the apparatus is insulated with extraordinary care, including the galvanometer and set of test-tube storage cells. Then, as a precaution against electrostatic effects, one end of the galvanometer is put definitely to earth by means of a wire soldered to the water supply. The galvanometer is enclosed in an iron case which is kept in connection with the earth, and affords a screen against external electrostatic effects. Referring to the diagram (see Plates), it will be seen that the effect is to put the lower plate of the sulphur condenser and one pole of the battery to earth as well, which insures that except for the small P.D. corresponding to the small current flowing, the greater part of the circuit and all the coils of the galvanometer are at zero potential. This has the effect of throwing the whole stress of insulation on the sulphur film, and on one insulating pole which supports the wire coming from the upper plate, and on two terminals of the reversing key.

The effect of accidental leakage, if any, is always observed by making all the connections except that leading to the top plate of the sulphur condenser, the wire simply hanging from the pole. Though this pole is of splendid flint-glass most carefully varnished and having a resisting length of about one metre, and is provided with an ebonite cross-arm about 20 centims. long, to the ends of which the wire is fastened, the insulation is seldom sufficient till the glass has been dried and the long, thin cross-arm of ebonite scraped. The connecting and reversing keys (see Plate 3, figs. 3 and 2) are formed of

pillars of ebonite of from 8 to 20 centims. long, and the two points of the reversing key requiring special insulation are made by placing ebonite cups on the ends of two pillars of fused quartz, each about 10 centims. long. The advantage of fused quartz as an insulator—where it is exposed to dusty air—lies not so much in its great freedom from surface effect, as observed by Boys ('Phil. Mag.' [5], vol. 28, p. 14), as in the fact that a small oxy-hydrogen flame can be applied to it without fear of breakage, and thus the insulation be made practically perfect for the day, without any rubbing or deranging of contacts. The advantages of the general arrangements are—

(1.) The points at which the insulation requires to be perfect are reduced to the fewest possible.

(2.) The system being definitely earthed at the galvanometer, gives a complete protection against electrostatic effects, which are very noticeable when this precaution is not taken.

(3.) The general insulation of the system is necessary when the evaluation of the galvanometer sensitiveness, or the capacity of the sulphur condenser, has to be determined, and it is a great convenience to secure this by disconnecting a single wire. The insulation of the "new galvanometer," by means of fused quartz rods, will be explained in its proper place (see p. 88).

The necessity for insulating the lower sulphur plate was well shown on one occasion, when it was omitted, to give rise to some trouble. Though this non-insulation produces no effect in so far as the applied voltage goes, yet it has practically the effect of short-circuiting the galvanometer through earth in one position of the reversing key and insulating one terminal of the galvanometer in the other. There are always minute voltages in the circuit, and these will cause a current through the galvanometer when it is short circuited. Hence, on reversing the key a throw will be observed which might be mistaken for a conduction throw due to conduction by the sulphur. As these voltages are very small, however, a sufficient insulation is easily obtained by a system of ebonite, paraffin and glass.

#### SECTION IV.

##### *On the Construction of Sensitive High Resistance Galvanometers.*

In a paper, "On the Measurement of High Specific Resistances" ('Phil. Mag.' [5], vol. 28, p. 466), one of us laid down what he considered to be the most important direction in which to look for improvement in galvanometers. Since then work at the subject has been going on, though with many interruptions, both in the workshop and laboratory. During the time that has elapsed, the matter has received a good deal of discussion, notably from Professor AYRTON, and Messrs. MATHER and SUMPNER ('Phil. Mag.' [5], vol. 30, p. 58).

As to the corrugations on paraffined ebonite pillars, our experience is that they are

not to be recommended with bare ebonite, unless the pillar be arranged (as should always be the case) so that they can easily be dismounted and cleaned up with a cutting tool on a lathe; mere washing or sand-papering does little good when very perfect insulation is required.

Theory, which is well understood, indicates the following conditions for maximum sensitiveness :—

- (1.) The magnetic force per unit current should be a maximum.
- (2.) The magnetic moment of each member of the suspended system should be a maximum.
- (3.) The mirror should, if possible, be so good that its defining power is only limited by its size; it should be optically perfect.
- (4.) The optical magnification should be a maximum.
- (5.) The astaticism of the suspended system should be a maximum.
- (6.) The field in which the suspended system moves should be zero when the astaticism is perfect, and the directional force entirely due to the unavoidable torsion of the suspending fibre. Since the astaticism is never perfect, and the field can never be zero, the torsion of the suspended fibre can only operate so as to reduce the sensitiveness, and must therefore be made as nearly zero as possible.

It is obvious that the above conditions are partially incompatible, and, as a matter of fact, it is the last condition which provides a starting-point.

The line of argument is this. In order to prevent changes of zero, we are compelled to use quartz threads. These threads are, however, very stiff. In order to prevent the stiffness being such as to seriously affect the sensitiveness, the threads must be very fine, and, consequently, the suspended apparatus very light. In order to go beyond this, it becomes necessary to determine to what point the optical sensitiveness can profitably be carried—or, what comes to the same thing, the limit of the angular value of the fluctuations of the zero. Under fixed conditions, the weight of the mirror will simply depend on the defining power required. The maker must take into account (1) the optical limit as to smallness, depending on the wave-length of light; and (2) the fact that the mirror must be thick enough neither to deform under its own weight, nor to deform owing to the freeing of internal stresses during its manufacture. Before exact theory can be applied to the construction of a galvanometer it is, therefore, necessary to fix on the weight of the mirror, and though, with the experience we have now acquired with magnetically and thermally screened instruments, we can form an estimate of the minimum weight of the mirror, we could not do so before the instrument was constructed. It was necessary, therefore, to proceed along the lines indicated by the general principles involved, and to make such alterations from time to time in the design as increased knowledge suggested.

An alteration which is now in progress is the application of stronger material than glass to the preparation of the mirrors. Even hard glass, considered as a mineral is

very weak, and is far surpassed in strength by many substances whose specific gravity is about the same. Fused quartz, for instance, is much stronger, and several discs have been cut from this substance, and are awaiting manufacture. We are also trying with slices of bloodstone, &c., and expect to obtain a considerable reduction in weight. It must never be lost sight of that the weight of the mirror is an unmixed evil. The mirror in use at present is of glass silvered on the back, with a diameter of 1.1 centim. and a weight of .0485 gram—it is slightly concave, having a radius of curvature of one metre, which was measured approximately. When we discuss the lines along which further improvements can be made it will be shown that owing to a peculiar mode of scale illumination which we have discovered, these dimensions can probably be a good deal reduced, but as our coils are wound at present, no advantage would be gained by effecting this reduction. The mirror is supported above the magnet system, but we are not sure that this is a good arrangement with such a large mirror—with a smaller one it would not matter. The definition of the mirror\* is so good that the image of a millimetre scale in it is read at a distance of 2.67 metres, by an improvised telescope and micrometer eyepiece, whose scale is graduated to .2 millim. Each division of this scale can be divided by eye into about 5 parts; and by means of the diffraction fringes surrounding the scale images, the latter can be located to this degree of accuracy in the micrometer.

With regard to the designing of the instrument we will take the conditions for maximum sensitiveness as laid down above, in order. We have experienced so much inconvenience ourselves when reading papers, in having to refer from lettering in the text to letters on the drawings, that we have prepared notes explanatory of the drawings to be placed beside them, and will endeavour here to give what explanations are required without making it necessary for the reader to refer to the drawings at every moment.

(1.) *The magnetic force for unit current should be a maximum*—resistance of the coil, or trouble and expense of winding, not to be considered. We have endeavoured to make an improvement in this direction, by using four pairs of coils, one above the other, instead of two, as has hitherto been the case. Preliminary trials showed us that we could hope to make the suspended system about 20 centims. long, and consequently the maximum diameter of the coils was approximately fixed. It will be noticed that the coils are much smaller than those ordinarily employed. This may be taken as a realization of a well-known principle, that when it is a question of resistance or quantity of wire, it is better to have many small coils than few large ones. We began by making a drawing of an instrument with eight tiers of coils, but abandoned it on account of the difficulty of making a suitable magnetic system of the necessary length. It is necessary to wind the wire regularly at the commencement of the winding, in order to get most turns in the most important part. We decided to wind the coils with cylindrical holes. The dimensions of the coils are shown in the

\* This mirror was made for us by our assistant, Mr. J. Cook.

drawing (Plate 1). It might possibly be worth while to use fine silver wire, and would certainly be advantageous to have the wire specially lightly insulated, but we are too far from manufacturing countries to be able to take advantage of such expedients. The wire employed by us has a diameter of  $\cdot 05$  millim. It was frequently necessary to make joints, owing to irregularities in the insulation. The best material for reinsulating the joints is a film of collodion, as it takes up less room than anything else we know of.

(2.) *The magnetic moment of each member of the suspended system should be a maximum.* This again is not purely a matter of design.

Our magnets were hardened circular discs stamped out of thin sheet steel. Each magnet consisted of two discs, one on each side of the support. Their dimensions were :

Diameter.	. . . . .	$\cdot 876$	centim.
Weight	. . . . .	$\cdot 0309$	gram each.
Thickness	. . . . .	$\cdot 008$	centim.

So that the weight of the suspended part is made up thus :

		gram.
8 discs weigh	. . . . .	$\cdot 2470$
1 mirror weighs	. . . . .	$\cdot 0485$
Wire and cement	. . . . .	$\cdot 0660$
		<hr/>
Total weight	. . . . .	$\cdot 3615$

So that the weight of the mirror is only about one-eighth of the whole weight, and the magnets form about five-sevenths of the whole weight.

At first we tried mica as a supporting material, but found it very much inferior to flattened aluminium wire, which can be twisted. A strip of mica, moreover, makes the combination more dead-beat ; which, with our method of observation, is equivalent to a reduction of sensitiveness.

We also rolled some sheet steel,  $\cdot 004$  centim. thick, into small cylinders as described by Professor LANGLEY, and compared the intensity of magnetization obtained with that of the small discs. The result is given in the accompanying table ; it will be noted the advantage is on the side of the disc. The experiments were made by Mr. POLLOCK. We dare say that better steel can be got ; but, unless Mr. ELLERY, F.R.S. (of Melbourne), had kindly come to our assistance, we should have had none at all.

TABLE IV.—Comparison of Magnetic Moments of Discs and Cylinders.

	Disc.	Cylinder.
Mass . . . . .	·0052 gram	·0045 gram
Diameter . . . . .	·5 centim.	·13 centim.
Length . . . . .	..	·46 "
Time of complete vibration . . . . .	·333 second	·385 second
Moment of inertia . . . . .	·00008	·000088
Intensity of field . . . . .	·26	·26
Magnetic moment . . . . .	·10957	·090137
Intensity of magnetization . . . . .	21·07	20·03

Condition (3) has been already treated.

(4.) *The optical magnification should be a maximum.* No part of our work has given us more trouble than the production of good scale images, and, in the end, in no part have we had more success. We began by using the telescope and scale set up in the usual manner, and, as usual, were troubled by want of illumination over some parts of the scale, and excess of illumination over others. The sources of light were also sources of heat, and caused the galvanometer to be unsteady, though it was well boxed in. We will not describe the many ineffectual experiments we made. Finally, the following plan was hit upon. A minute point of light (a kerosene lamp turned down very low) was placed edge-on about 2·9 metres away from the galvanometer. An image of this source was focussed on the centre of the galvanometer mirror by a large lens, 19·5 centims. in diameter, placed at a distance of 55 centims. from the mirror. Directly behind the lens, and between it and the mirror, was placed a scale, which, in our experiments, and after many trials, was made by coating a slip of glass with a film of Canada balsam stained with "nigrosine," and cutting divisions on this film on the dividing engine. The divisions were transparent, the general field being dark, and carefully kept so by placing the engraved scale in a proper recess cut in a black wooden screen. The advantage of the Canada balsam film is not obvious in this case, but the scale had been used in other experiments where double images gave trouble, and then the Canada balsam was of the greatest advantage in helping to prevent their formation, much in the same manner as M. CORNU'S varnish cures photographic plates of giving a halo round the image of a bright star ('Journ. de Phys.,' vol. 9, p. 275).

The film was, of course, turned towards the mirror, and the light fell upon it normally. It will be understood that by this we mean that the scale was a tangent to a circle described about the centre of the mirror. The object was, of course, to let the light pass through each division of the scale normally; and, since the scale was only about 10 centims. long, this condition was sufficiently fulfilled, and the scale did not require to be bent. Real images of the scale divisions were formed at about



260 centims. from the mirror. The reflected beam was, however, intercepted by the telescope, whose object-glass, consisting of a spectacle lens of 10 centims. focal length, was 267 centims. from the mirror. The image was observed in the micrometer eye-piece. When the light was not too bright, and everything well adjusted, the images were exceedingly bright on a dark field, and each was the centre of a system of the most perfectly defined and fine interference fringes. By moving the lamp slightly, these fringes can be got to arrange themselves somewhat unsymmetrically about the luminous image, and thus enable an observer to distinguish a particular fringe with certainty; one crossing the brightest part of the luminous image was always selected; and if the fringes were unsymmetrical one was always much the most sharply marked. The similarity of the tracings of the dividing engine was such that each division had a set of fringes, as nearly as we could see identical with the fringes of the images on each side of it, so that a particular fringe could be selected as the fiducial mark of the image, or the distance between two similar fringes could be taken as the distance between the millimetre divisions on the scale. At first the micrometer eye-piece was provided with a toothed or notched scale, but this not being sufficiently capable of sub-division, it was replaced by a scale divided on thin glass by a diamond, on the dividing engine, to .2 millim. A candle was then arranged so as to throw a suitable diffused light into the telescope, and, the micrometer scale presenting a diamond-cut edge, the coincidence of its divisions or otherwise with the interference fringes could be made out clearly and with great accuracy. The spider-line of the micrometer was not nearly so fine or so well defined as the interference fringes. By properly adjusting the fringes and illumination, everything became so distinct that it was much easier to read to micrometer scale divisions than it usually is to read with a lamp and scale to one division. We are quite sure that this method of illumination and scale reading will be found valuable by any one requiring to read small deflexions. The only points about which we would suggest caution are the following:—The light falling on the mirror must come from a source as small as possible, and a person setting up the arrangement for the first time would probably make the light much too bright and large for the interference fringes; the source must be a mere spark. The lens must be adjusted so as to be normal to the line joining the mirror and lamp, and this line must pass through its centre. The lens we used was an ordinary one, but it had good adjustments. The divisions on the Canada balsam or other varnish must be fine (we tried photographic transparencies, &c., instead, but they always looked woolly). The eye-piece of the telescope must be capable of very good adjustment. Ours was mounted on a fine tuning-fork stand by KÖNIG; it is no use unless the stand be very steady, and the adjustments, both vertically, horizontally, and in the altitude must be smooth and good. We made ours out of good brass tube without any difficulty. The source of light should be within reach of the observer at the telescope, in order that the final adjustment may be made by slightly moving the source, and by turning the lamp up and down till the best effect is obtained: this involves having

the reflected ray separated from the incident ray by an angle which is not too large. The method is suitable only for the observation of small angular deflexions, for we have not been able to engrave our scale with numbers finely enough to permit us to see the figures and divisions in the field at the same time. Consequently, a deflexion can only be observed by counting the images of the millimetre divisions as they flash past. With our present arrangements we can only count the divisions when they pass below a certain rate; when the whole deflexion amounts to more than about 20 millims., the divisions pass too quickly to be counted. However finely we might succeed in engraving numbers on the scale, we fear that the interference images would be too blurred to be read. The best method would be to omit every tenth division, say. We did not require to trouble about this, however, for the "old" galvanometer was always set up at hand, and, as soon as the deflexions became too large for the method of observation mentioned, recourse was had to it.

The diagram (Plate 4) will make the arrangement clear. A deflexion of one millimetre division is in angular measure  $38.6''$ , and since each millimetre division of the scale covered about 8 micrometer scale divisions, each divisible into 5 parts, we may consider that the smallest deflexion which could be read with certainty was say one-fortieth of this, or  $0.96''$ . Since the magnification depended on the adjustments, it varied slightly from day to day, but the general magnification was, as we say, such that the distance between two consecutive scale images covered from 8 to 9 micrometer scale divisions. We ought to add that the definition of the mirror was a good deal better than we have ever seen before in a mirror of about the same weight and dimensions. It was worked for us by Mr. Cook, together with a large number of similar mirrors, all about equally good. The best unworked glass we have tried was incomparably worse. The difficulty in making such thin mirrors out of glass arises from the fact that they always change their shape when they come off the polishing tool; but in our experience the change of shape is very regular, thus a flat mirror almost always becomes concave or convex; but it does not do so irregularly, and consequently the definition remains satisfactory. The glass, of course, is ground and polished on both sides. The window through which the light passes to and from the mirror, is a strip of patent plate-glass, selected by the method of observing the reflected images from the front and back, and cutting the glass so that it forms a prism of small angle along the top or bottom edge. Patent plate-glass can be got with fairly flat surfaces, which are, however, generally more or less inclined, and so in cases of this kind the glass must be cut in such a way that the inclination of the surfaces does not disturb the accuracy of the observations. For this method of selecting glass, we are indebted to Professor WRIGHT, of Yale.

(5.) *The astaticism of the suspended system should be a maximum.*

This is a most tiresome condition to satisfy, and we have nothing to add to what was said about it by one of us ('Phil. Mag.' [5], vol. 28, p. 458). In order to magnetize the system astatically, four electro-magnets had to be used; an attempt that was

made to screen half the magnetic system, while the other half was being magnetized, failed, even when the screening was attained by pushing half the system into a cylindrical hole bored in a thick soft iron bar. During the process of mounting the discs on aluminium wire, they generally got magnetized, and hence required to be demagnetized before the final magnetizing process was carried out. The demagnetizing was carried out by means of the arrangement of four similar electro-magnets, which were supplied with an alternating current. If we had foreseen the necessity, we should have provided these magnets with laminated cores; as it was, care had to be exercised to prevent them becoming so hot as to melt the paraffin used as a cement for the disc magnets. The final adjustments for astaticism were made by twisting the aluminium wire. This wire was only .35 millim. in diameter, and so the difficulty of obtaining a perfectly straight system of magnets of about 20 centims. long, and so astatic that the natural period of vibration was from 1.5" to 2", will be understood by anyone engaged in similar work. The natural period of vibration of two magnetized discs was a fraction of a second. We had hoped that it would turn out more easy to secure good astaticism with four-magnet systems than with two, but this hope was not justified by the event. The adjusting and mounting of the astatic system is the most difficult part of the manipulation; the final adjustment must be made by hand twisting, as described in the 'Phil. Mag.' (*loc. cit.*).

(6.) *The fibre must have a minimum torsional coefficient.* In plain English, the fibre must be as thin and long as possible; and it is, of course, much more important to have the fibre thin than long. The proper thickness was calculated from the results obtained by one of us in a paper on "Quartz Threads" ('Phil. Mag.' [5], vol. 30, p. 99, 1890), and the thread was then picked out by measurement with a microscope; a factor of safety of about 2 being generally allowed. As a matter of fact, the thread required is very fine, but not unmanageably so: pieces about 25 centims. long were generally used. We find that the thread can be fastened more securely by a little melted shellac than by hard paraffin; we have had several accidents from the thread slipping out of the paraffin. Of course shellac that has not been overheated or dissolved in alcohol, must be used. Care was always taken to use the thread in an untwisted state.

*On the General Design of the Galvanometer for High Degrees of Sensitiveness.*

The general principles had been arrived at in 1889 from experience with the old galvanometer, from which fair results had been obtained. The following is the result of our general experience.

(1.) It is of the first importance that the coils be adjustable to the suspended part, as well as the suspended parts to the coils. Unless provision be made for this it is practically beyond the powers of even the most skilful manipulator to make use of magnets properly filling up the coil space, and yet free to turn. This condition

determines a large part of the mechanical design. The coils must be carried separately, insulated on brass holders, for the nicety required is not to be obtained by the use of any softer or less rigid material. The framework of the instrument which holds the coils is made in two parts, which are scraped to fit; no screws or clamps are necessary to hold the two halves of the frame together; one half, containing half the coils, can be lifted up and carried away from the other half, the plane of separation being the plane containing the magnetic system. In order that the adjustment of the magnet system to the coils may be perfectly made, it is necessary to be able both to look through the axial holes of the coils and also into the narrow space (1.5 millim.) separating the two systems of coils. The method of mounting the coils will be clear from the drawings and description (Plate 1), but it is necessary here to indicate the general procedure. The coils, when wound, were embedded concentrically in rings of ebonite, a little paraffin being poured in and fastened both to the coil and ebonite by means of a hot wire. Four bars of fused quartz had been previously fastened as spokes into the ebonite—regarded as a hub—and by means of a centering apparatus devised by Mr. COOK, each coil with its ebonite and quartz was laid in a proper position in its coil carriage. This was a matter requiring much ingenuity, and was accomplished by means of the adjustable catches into which the ends of the quartz rods drop, and which are screwed to the carriage. The coil being in the centering apparatus, the catches of the carriage are adjusted to the quartz spokes; the catches are then made fast to the carriage, and then the quartz is made permanently fast to the catches by means of a little plaster of Paris. The quartz spokes are like nails, *i.e.*, they have heads, and are fastened to the ebonite rings by being pushed through them from inside before the coil is centred and cemented by paraffin, which also, of course, cements the head of the quartz spoke. Each coil carriage is screwed to the frame by separate screws, which allow a little latitude for final adjustment to the magnetic system when this is suspended. The detail of the whole of the devices for adjusting coils insulated by quartz rods, we owe to Mr. COOK, and we are not sure that the system would succeed with less perfect workmanship than he put into the construction. The arrangement proved in practice to be everything that could be desired.

(2.) The apparatus carrying the coils and magnet system must be absolutely separate and independent of the parts carrying the controlling magnets. This is a condition of the first importance—however good all the other arrangements may be, they will fail in practice unless this condition is fulfilled. We have tried over and over again with the controlling system more or less connected to the suspended system, but have never had any success with such an arrangement, however massive the brass work. This condition may be regarded as the result of all our experience. At one time we tried supporting the coil system on rubber bungs mounted with more or less elaboration, and on discs of rubber mounted in different ways; but observations with a mercury trough convinced us that with our concrete and asphalt block floors, the rubber always

did more harm than good. At present the instrument is mounted on a hard smooth slab of concrete, which reposes on a sandstone pillar resting on the concrete on which the floors are laid. The coil system is mounted on a sheet of ebonite supported by insulators on the concrete slab, and the controlling magnet system is supported by leaden pillars passing through the ebonite without touching it, and also resting on the concrete slab. The natural stiffness of the slab, or rather its inertia, is much increased by the fact that it carries the magnetic shield of cast iron weighing about three hundred pounds. This materially lessens any tendency there might be to produce disturbance in the suspended system by adjusting the controlling magnets.

*The Magnetic Control.*—The whole secret of success lies in this. Instead of regarding the control as a subsidiary part of the apparatus, it must be regarded as the most important part, and must be capable of the finest adjustment. We have found it advisable to use the controlling magnets at such a distance that the residual field is due to them, and not to the earth. In this case, small changes in the direction of the earth's field produce less effect than when the residual field is that due to the magnetic action of the earth. We have a simple but important improvement to report in the matter of control. It turns out that when the sensitiveness is very high, the uniformity of the magnetic field becomes very important. When the field is not sufficiently uniform, the following fatal effect is observed. We will suppose that the earth's field is in excess, and that the magnets are in the magnetic meridian. The control magnet, we will suppose, is lowered gradually; finally, a point is reached at which the period is fairly long, and the suspended part, if nearly at rest, behaves apparently well; now let it be caused to vibrate (in practice, the control can never be lowered without causing the suspended magnets to vibrate more or less). It is always noticed that if the excursion rises beyond a certain very small value, then the suspended magnet swings round perhaps  $70^\circ$  or  $80^\circ$ , and takes up a new position of greater stability than the old one. In order to bring it back the control magnets have to be rotated, with the invariable effect of making the suspended magnet swing past the north and south position, and take up a more or less symmetrical position on the other side. Attempts to bring the needles back by moving external magnets, or working damping arrangements, seldom succeed, and in the end the controlling magnet has usually to be raised, and the tiresome business begun afresh. We have wasted many days over this untoward phenomenon. Suppose, however, that the difficulty is apparently surmounted and the image got on the scale and fairly steady, and observations begun. It is always found that after a time the needle begins to drift, and finally goes over to one of the side positions. This was first noted by Mr. POLLOCK with the old galvanometer in 1889. The cause of these effects is not far to seek. The field produced by a simple control magnet is never uniform. In such a long system as ours, and with the controlling magnet at the top, the lower suspended magnet is directed by the earth's field, and the upper one by the control, the centre ones being probably in a nearly

neutral field. The diagram (in MAXWELL, 'Elec. and Mag.,' vol. 2, fig. 15), shows how very far from uniform the field is, at or near the neutral point. If the magnetic system be rotated through a very small distance, it comes to a place where the resultant field is differently directed, and then sails away till a new position of equilibrium is attained. The usual practice of considering the field as only influenced by the earth and controlling magnet, and of regarding the suspended magnet as without influence, is fallacious. The direction of the lines of force depends on three things, the earth, the controlling magnet, and the suspending magnet. MAXWELL'S diagram, fig. 15, represents the case of the discovery well, but the matter is complicated by the fact that the resultant field of earth and control magnet is far from uniform even before it is distorted by the suspended magnet.

It seemed likely that much of the difficulty would be removed by making the residual field more uniform, and with this object two additional and similar control magnets were introduced below the suspended system, and adjusted by trial till they were as nearly as possible symmetrically placed with respect to it and the upper adjustable system. The magnets were of the dimensions and at the distances shown in the drawing (figs. 1 and 2), and it was expected that they would produce a field of surface uniformity sufficient for the purpose, after the manner that the HELMHOLTZ coil arrangement produces a solid uniformity (MAXWELL, vol. 2, fig. 19). The arrangement figured was set up as a trial, but as its success was immediate and complete, we never went on to the selection of magnets of proper length—a step we expected to have to take. Since using the arrangement all the wearisome instability and trouble has been diminished so much that we now adjust our sensitiveness and take observations with no more concern than if we were operating with a wooden galvanometer for a rough resistance balance.\*

We must not forget to mention the prime importance of having the fine movements of the adjustable part of the control—the upper magnets in our case—as good as workmanship can make them. The rough adjustment for distance is made by sliding the magnets, screw system and all, up and down. The fine adjustment is by means of an excellent nut and fine screw thread—a device described in 1889. The adjustment in azimuth is by means of the lever and screw device, the rough adjustment by releasing a clamp and twisting the magnet carriage. As the magnets and nut together weigh several pounds, we should have done better had we arranged a counterpoise, so that the freedom of rotation of the screw should not be affected by the great pressure on it, as is the case at present; for, though the bearing surface of the nut was well ground, and was kept well oiled, still, on screwing the magnets up, the friction was enough to slightly twist the wide and thick brass tube, and so to displace the magnets in azimuth.

\* Oct., 1893.—After more than a year's experience we have never had the slightest difficulty in obtaining the sensitiveness desired since we made the field uniform.

We believe that it is not only feasible but advisable to further increase the uniformity of the controlled field.

*Insulation of the Coils from the Frame.*—If the quartz is protected from dust it insulates very well, better than anything else we know of in places which can not be got at constantly for treatment. After being in use for some months, the total insulation of the coils and terminals from the frame was  $1.2 \times 10^9$  ohms, the measurement being made by means of an electrometer. The method adopted for insulating the terminals and connecting wires does not differ much from ordinary practice. The terminals are of corrugated ebonite, of slender section; the wire passing into the terminal from the coils passes up the ebonite column without touching it, till it reaches the binding screw. The ebonite terminals themselves are screwed into the glass forming the front and back of the galvanometer, and the insulation is improved by drying and varnishing this glass. Where the wires pass from coil to coil inside, they are supported as little as possible; but where supports can not be avoided, these are made of needles of fused quartz. All the connections are permanently soldered, and it is to be noted that we have carried out in insulating the coils what we consider to be an essential condition of success, viz., the use of a variety of insulating substances.

There are 12,280 turns in each coil.

Total turns, 98,240.

Total resistance, 43,985 ohms, at 23° C.

*Screening from Electrostatic Effects.*—We expected to have to interpose a film of mica silvered on one side, between the coils and magnetic system, but this has turned out to be unnecessary. The insulation would certainly suffer if the magnets have to be screened.

*Capacity of Coils.*—The total capacity of the coils and terminals, the inner casing being put to earth, is  $8 \times 10^{-5}$  microfarad, by measurement.

*Avoidance of Thermo-electric Effects.*—When the instrument was first set up, some small pieces of stiff German-silver wire were used to pass down inside the ebonite terminals. On short circuiting enormous thermo-electric effects were always noted even when all precautions to secure a constant temperature had been taken. These effects could only be removed by replacing the German-silver by copper, and by electroplating the brass binding screws with copper, and by soldering all joints (except the contact at the binding screws) right up to the galvanometer key.

*Screening from Air Currents and Convection Currents due to difference of Temperature.*—It was found necessary to seal the coil cases with soft wax, so that the interior of the galvanometer becomes almost air-tight. The sealing is easily accomplished, because, as has been mentioned, there are four glass sides, and the wax was run round the edges of the glass. Thermal effects were guarded against by enclosing the whole apparatus in a mill-board box, coated with tin-foil inside and out, and very

conveniently built up around the heavy gunmetal frame carrying the controlling system. The iron slabs of the magnetic screen were also tin-foil coated and a roof was erected on them of mill-board covered with tin-foil. This roof had holes cut in it for the connecting wires to come through, and for the stem of the controlling system. All these precautions were the result of attempts to remedy faults as they made their appearance.

*Magnetic Screen.*—Four iron slabs were prepared from cast iron and arranged so as to form a symmetrical box, without top or bottom, round the instrument. The screening was not very perfect, and if we could have got soft iron we would have used it. However, the improvement made by this screening was very great, and it was no use trying to improve it by cast iron, for we used as much as we could trust the concrete slab to carry, and put it as near to the instrument as possible. It was supported on a wooden frame. When further improvements are made, the most important of them will be in increasing the magnetic screening, even if it takes half a ton of soft iron. The approximate reduction of the earth's horizontal field due to our screen is from 26 C.G.S. to about one-twentieth of this. The screen weighed 300 lbs.

*Residual Fluctuations of Zero.*—These always make their appearance when the single steady deflexion is above 1 micrometer division for  $5 \times 10^{-11}$  ampère. We have endeavoured to trace the cause of this fluctuation. We made a number of experiments by heating the instrument unequally by means of gas furnaces placed in different positions with respect to it, with the result that we discovered that the temperature differences had a considerable effect, but not enough to account for the fluctuations. We habitually use the instrument in a room of fairly constant temperature, and the method of illumination cannot be charged with giving rise to the variations; for the lamp may be turned up so as to radiate, say, a hundredfold as much energy without producing any increased effect. The only radiation reaching the interior from the lamp is that which can pass through the fine scale divisions, and this all impinges on the surface of the mirror. The fact that the instrument is practically air-tight, precludes the theory that external currents of air cause the effect. Besides, there is the mill-board box coated with tin-foil, and outside that the iron and mill-board box.

It remains to consider variations in external magnetic force, and it is to these variations that we attribute the fluctuations observed. Our reasons are: (1) The magnetic screen made the needle much steadier. (2) The residual unsteadiness varies very much from day to day; on some days it is impossible to use the instrument with a period of more than 10 sec., and on others the zero is absolutely still and constant during, say half-an-hour, when the period reaches 25 sec. or 30 sec., and, of course, it always happens that these periods of magnetic peace only occur when we want to measure comparatively low resistances. The fluctuations have, moreover, all the appearance of being due to general causes, for they appear equally at night-time when



nothing in the Laboratory is being moved, and when there is no traffic in the road. They are always bad on a windy day; but this may possibly be attributed to small changes of barometric pressure occurring from wind pressure. We are placed at about 150 yards from a road along which a steam tram runs, and every time a tram comes past, the needle moves about violently; in fact, we often obtain the first indication of the approach of a tram from the motion of the needle. All these drawbacks can only be eliminated by increasing the efficiency of the magnetic screen, and this is therefore the next step to take.

*Method of Observation.*—In order to obtain the maximum reading for a given current, we always obtain a double deflexion, and read the first elongation of the needle. Whether this elongation be produced by the current through the sulphur or by the derived circuit from the Clark cell, there is practically no induction in the circuit, except that in the galvanometer itself. If the derived circuit current be adjusted to give the same throw of the galvanometer as the leakage current, we consider that the currents must be the same.

As an example of the behaviour of the instrument, we will give one complete set of experiments, at a normal sensitiveness, taken on October 17, 1892, a very unsteady day.

TABLE V.—Throws of Galvanometer in Micrometer Scale Divisions.

Date.	Voltage.	Resistance.	Battery position.	Double deflection.	Amplitudes from special experiments.	
					1st-2nd. elongation.	2nd-3rd elongation.
Oct. 17, 1892	$2 \times 10^{-5}$ , Clark	$1.044 \times 10^6$ ohms	+ to upper terminal			
"	"	"	"	A—B, 8 divisions	7	5
"	"	"	"	B—A, 7.5 "	8	6
"	"	"	"	A—B, 8 "	8	6
"	"	"	"	B—A, 8 "	7.5	5.5
"	"	"	—to upper terminal	A—B, 7.5 "	Not	taken
"	"	"		B—A, 8.0 "		
"	"	"		A—B, 8.5 "		
"	"	"		B—A, 7.5 "		

Mean deflection,  $7.9 \pm .3$  micrometer divisions.

Period of a double vibration, 14.5 sec.

*Values of  $\rho$ .*—The ratio of the 2nd elongation to the 1st.

$$(1) \rho = 7/5 = 1.40,$$

$$(2) \rho = 8/6 = 1.333,$$

$$(3) \rho = 7/5.5 = 1.273,$$

$$(4) \rho = 7.5/5.5 = 1.364.$$

Mean,  $\rho = 1.3425 \pm .042$ .

If  $\phi$  be the steady deflection corresponding to the throw  $\theta$ , then (MAXWELL, II., § 745)

$$\phi = \frac{\rho\theta}{1 + \rho}.$$

Now  $\rho = 1.3425$ .  $\theta = 7.9$ , and therefore  $\phi = 4.53$ . But  $\phi$  is the deflection on reversal, hence deflection from the zero for the current employed is 2.26 divisions. The current is  $C = E/R$ .

$$\begin{aligned} &= \frac{2}{10^5} \times \frac{1.43}{1.044 \times 10^6} \text{ ampères,} \\ &= 2.74 \times 10^{-11} \text{ ampère.} \end{aligned}$$

Hence a current of  $2.74 \times 10^{-11}$  ampère produces on reversal a throw of 7.9 micrometer divisions. Leaving the damping out of consideration, this is the same as a current of  $3.5 \times 10^{-12}$  ampère, producing a throw of 1 micrometer division on reversal. Taking damping into consideration, this would be slightly increased, since the damping is less the smaller the deflection. Now on several occasions (though not on this particular one) in times of exceptional magnetic quiet, readings could be taken to one-fifth of a micrometer division. If, therefore, we consider that a throw of one-fifth of a micrometer division is the least observable, it follows that we could detect a current of one-fifth of the above, viz.,  $7 \times 10^{-13}$  ampère, and this with a time of swing of only 14.5 sec. In practice we do not think that a current so small as  $7 \times 10^{-13}$  ampère could be detected with certainty, even when the galvanometer is steady, because of the small thermo-electric effects that are always exhibited by the contact keys, and which would probably give rise to much greater currents than this.\* One of the most important matters awaiting solution is the construction of a reversing key, which shall be free from contact effects.

If we estimate the current required to produce a steady single deflection of 1 micrometer division, we find it is

$$C = \frac{2.74 \times 10^{-11}}{\frac{1}{2}\phi} = \frac{2.74 \times 10^{-11}}{2.26} = 1.21 \times 10^{-11},$$

and the current which would produce the smallest perceptible deflection is one-fifth of this, or  $2.4 \times 10^{-12}$  ampère.

On the same day a similar series of experiments were made with currents corresponding to  $5 \times 10^{-5}$  and  $10 \times 10^{-5}$  part of the voltage of a Clark cell.

\* Oct., 1893.—Since then we have habitually measured currents of this order.

The following table is a summary of the results of these and other observations, and shows how necessary it is to calibrate the galvanometer for each particular throw, when these are not large :—

TABLE VI., giving Summary of Experiments made on October 17, 1892 ;  
October 25, 1892 ; and December 1, 1892.

*Galvanometer period*, 14·5 sec. on October 17, 21 sec. on October 25, and 26 sec. on December 1. 8 Micrometer divisions cover 1 millim. in the scale image.

Date.	Voltage in terms of Clark cell.	Current, in ampères.	Mean throw on reversal, in micrometer divisions.	Sensitiveness for one division on reversal, in ampères.	Values of $\phi$ for double deflexions. $\phi = \frac{\rho\theta}{1+\rho}$ .	Sensitiveness for one division steady deflexion, in ampères (i.e., current re- quired to produce one division steady deflexion).
Oct. 17, 1892	$2 \times 10^{-5}$	$2.739 \times 10^{-11}$	7.9	$3.5 \times 10^{-12}$	4.53	$1.21 \times 10^{-11}$
" "	$5 \times 10^{-5}$	$6.85 \times 10^{-11}$	18.6	$3.68 \times 10^{-12}$	10.32	$1.32 \times 10^{-11}$
" "	$1 \times 10^{-4}$	$1.36 \times 10^{-10}$	35.3	$3.85 \times 10^{-12}$	18.6	$1.46 \times 10^{-11}$
Oct. 25, 1892	$1 \times 10^{-5}$	$1.37 \times 10^{-11}$	10.5 (mean of 14 observations)	$1.31 \times 10^{-12}$	6.6	$4 \times 10^{-12}$
Dec. 1, 1892	$5 \times 10^{-5}$	..	51.8	$1.32 \times 10^{-12}$		
" "	$3 \times 10^{-5}$	..	28.7			

This table requires little comment. If the sensitiveness were reckoned in terms of the least visible deflexion, it would appear to be five times greater. The deflexions are obviously rather greater for smaller currents than for larger. If we consider what has been said about the state of the resultant field, even under such a fairly strong control as this, it appears that any simple galvanometric law is not to be expected. It is not worth while exhibiting any other tables of sensitiveness, for, though all the sulphur observations might be used for the purpose, in general the sensitiveness for steady deflexion was not required, and was not calculated.\* In the tables giving the results by the measurements of the sulphur resistance, the sensitiveness per double deflexion (throw) is given, corresponding to each set of observations. For the sake of rapidity of observation, the sensitiveness was adjusted to suit the work in hand. We do not wish to attempt any comparison between this instrument and those employed by other experimenters : our object was to attempt to combine a high degree of sen-

\* Note added September 23, 1893 :—

We have lately had occasion to use the galvanometer at the highest degree of sensitiveness conveniently attainable, in order to study the conduction in films which could not be made very thin. For this purpose the period was raised to 25 sec. The terrestrial magnetic conditions were only fairly steady.

sitiveness with ease and certainty in use, and in this we consider we have succeeded to an extent commensurate with our immediate wants. We do not see our way to the suggestion of any material simplification in design, without sacrificing convenience

The voltage was supplied from the terminals by a two-tenths ohm coil, in series with 100,000 ohms and the Clark cell. The following are the readings :—

Galvanometer reversed from A - B. Throw, 18 divisions.

"	"	B - A.	"	16	"
"	"	A - B.	"	17	"
"	"	B - A.	"	20	"
"	"	A - B.	"	19	"
"	"	B - A.	"	20	"

Mean . . . . 18·3 micrometer divisions.

Battery reversed.

Galvanometer reversed . . A - B. Throw, 27 divisions.

"	"	B - A.	"	24	"
"	"	A - B.	"	24	"
"	"	B - A.	"	26	"
"	"	A - B.	"	23	"
"	"	B - A.	"	26	"

Mean . . . . 25 divisions.

Key in circuit only . . . A - B. Throw, 0 division.

"	"	B - A.	"	1	"
"	"	A - B.	"	0	"
"	"	B - A.	"	0	"

Coil plugs inserted, so as to allow for resistance of terminals, &c.

Galvanometer reversed . . A - B. Throw, 2 divisions.

"	"	B - A.	"	4	"
"	"	A - B.	"	3·1	"
"	"	B - A.	"	2·5	"

Battery reversed.

"	"	A - B.	"	0	"
"	"	B - A.	"	2	"
"	"	A - B.	"	2·1	"
"	"	B - A.	"	3	"

Mean . . . . 2·3 divisions, say.

Hence, mean deflexion for a resistance of ·2 ohm between the points of derivation is 19·3 divisions. The current is less than  $\frac{2 \times 1.435}{10^{12}}$  ampères, since the megohm was in series with the galvanometer. The sensitiveness, therefore in ampères per scale division, is

$$\frac{1.435 \times 2}{1.93 \times 10^{13}} = 1.48 \times 10^{-13}.$$

On a really steady day, ·2 micrometer division can be read with absolute certainty; hence, if this condition had obtained on this occasion, the sensitiveness for least observable deflexion would have been  $3 \times 10^{-14}$  ampère.

of adjustment. The improvements which can still be made are (1) greater strength in the support of the controlling system ; (2) increased fineness of adjustment of the controlling system ; (3) better arrangements for twisting the suspended fibre when the controlling system is mounted ; (4) increased uniformity of residual field ; (5) more perfect magnetic screening ; (6) numbering the divisions of the millimetre scale ; (7) observing in some place not affected by traffic along streets or roads. Of these, (5) and (7) are much the most important.

Perhaps we ought to add that we are quite aware that at least as high a degree of sensitiveness as we have attained, may be got out of a much less elaborate instrument—on occasion. We have obtained such results ourselves with the “ old ” galvanometer. The point we wish to make is not that the sensitiveness is extraordinary, but that, such as it is, it is daily and hourly available with all the ease and certainty of observation generally associated with instruments of, say, a thousand times less sensitiveness.

## SECTION V.

### *Account of Experiments on Sulphur in Chronological Order.*

The first experiments were made with the arrangement of plates figured in the ‘ Philosophical Magazine ’ [5], vol. 28, Plate 14, and the diagram of connections was the same as is given in the same volume, p. 470. The plates were of brass truly faced by scraping to a surface plate : they were first platinated by ROSELEUR’s method, and afterwards gilt and burnished many times. The object of the continual gilding and burnishing was to make the gold film as solid as possible ; for it was found that if the film was at all spongy, the sulphur penetrated it at a high temperature and acted on the brass below. There were also some few spots that seemed disinclined to gild. These spots were finally drilled out and plugs of gold were inserted by a dentist’s apparatus. The result was never perfectly satisfactory. The flatness of the plates, however, was preserved to such a degree that the mere contact of the upper clean plate was strong enough to lift the lower one, which weighed about 2·75 kilograms. These plates were prepared by Mr. POLLOCK. A film of sulphur was got between the plates by placing the lower one in the gold dish, and pouring in sufficient melted sulphur to cover it to a depth of about half a centimetre. The sulphur used was in this—as in every subsequent experiment unless the contrary be specifically stated—the sulphur recovered by the Chance process, distilled three times in hard-glass retorts. A subsequent examination of the film showed that it was almost entirely monoclinic containing less than 1 per cent. of insoluble sulphur. The screws used for separating the plates had undergone a slight modification, so that the effective area as deduced from a series of measurements by a fine pair of vernier callipers was 193·3 sq. centims. From this it was estimated that the actual area was 190·3 sq. centims.—3 sq. centims. being taken up by bubbles, and by a corner of the film which was

broken away in cutting down into the sulphur round the plates in order to increase the surface resistance. We may call the area 190 sq. centims. The micrometer screws were adjusted so as to leave a film space of .05 centim. This was therefore the thickness of the film. So much difficulty was experienced in screwing the screws back that it was determined for the future to use some other method of separating the gilded plates. During the attempts that were made to get a value of the resistance of the film, several facts came to light on which our subsequent practice was founded.

The first was with respect to the necessity for insulating every part of the apparatus. Our connecting keys proving unfit for such high resistance work, new ones were made out of rods of ebonite about 20 centims. long, and were so arranged that it was easy to get at the ebonite in every part for the purpose of scraping it with bits of broken glass—a very effective way of cleaning it. It was also found that there was a considerable amount of surface conductivity over the sulphur, and we finally were obliged to use phosphorus pentoxide as a drying agent, anything less active failing to give satisfactory results. The battery of test-tube storage cells was reinforced by a water battery\* consisting of zinc and copper plates, as described by Professor ROWLAND ('Phil. Mag.' [5], vol. 23, p. 303).

In the final experiment with the film under consideration, a voltage of 551 was used. It was measured—not very accurately but sufficiently so—by the simple means of charging a fraction of a microfarad condenser with it, and observing throws with a galvanometer. Another division of the microfarad was afterwards charged by 40 Clark cells, and the throws similarly observed.

The galvanometer employed was the one described by one of us in the 'Philosophical Magazine,' vol. 28, which we now call the "old" galvanometer. It had a sensitiveness of 1 scale division for  $1.44 \times 10^{-11}$  ampère, with a deflexion of about 23 scale

\* This battery is very convenient when it is once got into good order, but it is not suitable for work of this kind, because many days often elapse between consecutive measurements, and then, as a rule, a good deal has to be done to the battery to get it into good order again. For this reason we no longer use it. The little storage cells are also a great source of trouble and annoyance. A battery of storage cells, to be reliable, requires much attention and ought not to be too small. However, as this battery was first set up in 1887, and is still (October, 1893) in use, perhaps we ought not to complain. The result of our experience is that if we had to make such a battery again, we would attend to the following points: (1) The test-tubes might be advantageously replaced by strong glass cells—of square section, and not less than 3 centims. on each side—inside. (2) The lead plates should be at least 3 millims. thick. (3) They should be formed plates—not pasted in any way. (4) The tops of the cells and the places where the plates bend over should be dipped in marine glue. (5) The cells should not be crowded together, so that they can only be examined by being taken out. It is a mistake to save space at the expense of the satisfaction of this condition. (6) The plates should be separated in each cell by a substantial partition of celluloid or other suitable substance, and it is better to put up with an increased resistance than to cut away most of the partition for the sake of reducing it. (7) The terminal wires should be thick and well coated with marine glue or gutta-percha. (8) The cells should be enclosed in a space which can be shut up, so as to prevent excessive evaporation. (9) The lead plates should not approach the bottom of the cells nearer than about 6 centims.

divisions. Since it was described in the 'Philosophical Magazine,' and before it made its appearance in connection with this work, one of the coils developed a fault. It was therefore replaced by a coil of much fewer turns and only a few hundred ohms resistance, which we happened to have by us. The diminished sensitiveness is due to this cause. It was rather unstable and consequently difficult to observe; owing to this, for the sake of security we have considered 10 scale divisions, instead of one, as the limit of effective sensitiveness. We could detect no current whatever through the sulphur with this instrument and the voltage mentioned.

The resistance is therefore certainly greater than

$$\frac{551}{1.44 \times 10^{-10}} = 3.83 \times 10^{12} \text{ ohms at (say) } 18^{\circ} \text{ C.}$$

And the specific resistance is greater than

$$\frac{190}{.05} \times 3.83 \times 10^{12} = 1.5 \times 10^{16} \text{ ohms (say) } = 1.5 \times 10^{25} \text{ C.G.S.}$$

This will be discussed in connection with other results.

The capacity of the condenser formed by the sulphur plates was measured ballistically, or rather it was compared with the capacity of the same condenser, when the film had been removed and the plates separated to the same distance by bits of quartz needles. As this was an operation requiring time, one of the divisions of the microfarad condenser was used as a step. The result was that the specific inductive capacity arrived at was 3.5, which is about the mean of the values obtained by BOLTZMANN and WÜLLNER, who probably used sulphur of this kind, *i.e.*, melted at a temperature not much above the melting-point, without any special precautions to ensure solubility. At this time we were not examining sulphur with respect to the resistance of its modifications, and the specific inductive capacity was taken as a check in order to be sure that the plates had not come apart. We were also anxious to see whether we could detect any sort of excessive current on charging, but the value obtained showed us that the closing current was quite normal. Of course the sulphur had been frequently stressed by the repeated application of a large voltage to insure its having reached a steady state. These experiments were partly preliminary; and we took no notice of the change of resistance on reversal, or of the action of time, for the very good reason that we got no measurable deflexion even with the large voltage applied.

On taking the plates apart the film was almost perfect, and showed no sign of staining or of any action at all. The gilding of the plates, however, showed a few black specks where the copper had been acted on through the (spongy?) gold. This is the only objection we have to this series of experiments. The results were afterwards confirmed in so far as resistance goes by the new galvanometer.

The next two series of experiments failed, owing to the spots on the plates becoming more and more marked, and though some of the results are probably unvitiated by this source of error, we have decided to leave them on one side. So far as they went they were very variable, the variability probably depending on the action of the current itself and on the time. To remove the source of uncertainty, due to the perforation of the gold film, we reluctantly decided to prepare two new plates, and after some difficulty obtained two brass castings, which appeared to be perfect after they were shaped. These were then gilt very heavily—several ounces of gold must have been deposited on them—and the gilding, burnishing, and regilding were carried out as before. A preliminary experiment was then made to find if the sulphur had any action, when it turned out that though the spots were fewer and smaller than before, they were still present. This induced us to put the plates on one side, and some thick aluminium having by this time come to hand, two new plates were made of aluminium. These plates have remained in use ever since. They were got flat on the surface plate, and we trusted to keeping them apart by bits of quartz thread instead of screws, a process that turned out quite satisfactory. A large number of experiments were made on bright and scraped pieces of aluminium, with the object of finding out whether sulphur had any action on the plates during the time when and at the temperature at which they were exposed to its action. No trace of action having been discovered, even when the sulphur was burned on the plates, it was decided that they could be used with confidence. The upper plate was provided with an aluminium handle attached to it by aluminium screws; the handle was always removed during the electrical measurements. The dimensions of the plates were obtained by a series of measurements with the vernier callipers, which will be set down here, as the other absolute measurements depend upon them. These callipers had been found on a previous occasion to agree with the standard metre within very narrow limits.

*Top Plate.*

MEASUREMENT in terms of the scale of brass callipers by ELLIOTT BROS. Corners named A, B, C, D, in order. Temperature, 24·8° C.

*Side A-B.*

	centims.
At one end . . .	12·361
At middle . . .	12·364
At other end . . .	12·363
<hr/>	
Mean . . .	12·3626

*Side B-C.*

	centims.
At one end . . .	12·653
At middle . . .	12·652
At other end . . .	12·651
<hr/>	
Mean . . .	12·652



*Side A-D.*

	centims.
At one end . . .	12·651
At middle . . .	12·652
At other end . . .	12·651
<hr/>	
Mean . . .	12·6513

*Side D-C.*

	centims.
At one end . . .	12·367
At middle . . .	12·367
At other end . . .	12·367
<hr/>	
Mean . . .	12·367

*Mean breadth of top plate,*  $\frac{12·3626 + 12·3670}{2} = 12·3648$  centims.

*Mean length of top plate,*  $\frac{12·6520 + 12·6513}{2} = 12·6516$  centims.

*Area of top plate, 156·43 sq. centims.*

*Dimensions of Bottom Plate.**Side A-B.*

	centims.
At one end . . .	12·360
At middle . . .	12·361
At other end . . .	12·362
<hr/>	
Mean . . .	12·361

*Side B-C.*

	centims.
At one end . . .	12·646
At middle . . .	12·645
At other end . . .	12·644
<hr/>	
Mean . . .	12·645

*Side D-C.*

	centims.
At one end . . .	12·365
At middle . . .	12·367
At other end . . .	12·365
<hr/>	
Mean . . .	12·366

*Side D-A.*

	centims.
At one end . . .	12·657
At middle . . .	12·656
At other end . . .	12·656
<hr/>	
Mean . . .	12·656

*Mean breadth of bottom plate,*  $\frac{12·361 + 12·366}{2} = 12·3635$  centims.

*Mean length of bottom plate,*  $\frac{12·645 + 12·6563}{2} = 12·65065$  centims.

*Area of bottom plate . . . . 156·40 sq. centims.*

*Mean area, both plates . . . . 156·415 „*

*Thickness of top plate . . . . .58 centim.*

*Thickness of bottom plate . . . . .32 „*

The preparation and testing of these different plates lasted from April till October,

1891. On October 6, 1891, a film of recovered sulphur, four times distilled and .022 centim. thick, was got between the plates, and a long series of experiments commenced with it. Amongst other experiments the amount of residual charge was measured, and, on November 12, 1891, the film was heated up to near the melting point. All the results obtained were so irregular that we could not draw any conclusions from them, and several circumstances led us to suspect that the film had been pierced by electric stress on October 15, with a voltage of 712. The plates were taken apart on January 6, 1892, when it was found that the film no longer adhered to the aluminium plates, and that a discharge had passed at some time or other, forming a lump of dark-coloured substance, and burning a hole in both aluminium plates. All the results obtained between October, 1891, and January, 1892, have, therefore, been rejected, with the exception of the following, all of which were afterwards confirmed, and which we had reason to think were not affected by the piercing of the film.

(1.) Before the film broke down with the voltage of 712 it had been exposed to voltages of about from 648 to 684 volts, giving rise to a small conduction, which was intermittent. In the first experiment a deflexion of 58 divisions was obtained with the battery in one direction, and of only 20 divisions when it was reversed; on reversing again, a deflexion of 68 divisions was obtained. These results are similar to others afterwards obtained with much smaller voltages, and are of importance as showing that the properties of sulphur, considered as a conductor, do not undergo any great qualitative change when the voltage per unit length is increased nearly to the breaking-down point.

The specific resistance of the sulphur, if we take 40 divisions as the average deflexion, is about  $6.6 \times 10^{22}$  C.G.S.

The film contained an unknown amount of insoluble sulphur, but this resistance is less than any other observed by us at the same temperature ( $18^{\circ}$  C.), while it is known that the amount of insoluble sulphur present could only have been very small as the film was cooled slowly. It will be shown that in general the resistance appears to diminish with an increased voltage, so that very possibly the small resistance observed in this experiment may be due to the high voltage employed, or, rather, to the great electric force in sulphur.

(2.) The sulphur was not cut away from the plates in this instance, but extended from the upper plate to the sides of the gold dish. After the film had been broken down, or, rather, after the time at which we consider it had been broken down, the resistance, as we have said, became very irregular. In seeking for the cause of this we examined several possible explanations, and, amongst them, the influence of surface action. The surface leakage, in this case, must have occurred between the upper plate and the sides of the gold dish, and it was thought that the surface resistance could be increased temporarily by scraping the intermediate sulphur surface. This was done without producing any change in the apparent resistance. The following

experiment was then made in order to reduce the surface conductivity (if it existed) to zero. A number of thick rods of fused quartz were prepared, carefully cleaned and heated to redness; when they were sufficiently cool, *i.e.*, when they would just melt the sulphur, they were arranged to lie in the surface of the sulphur between the upper plate and the gold dish, and were caused to lie half embedded in the sulphur. Now, if any surface conductivity exists in the sulphur, it will be checked where the surface of the sulphur is interrupted by the quartz—in other words, the current would have to climb over the exposed part of the quartz rods. Now, the surface conductivity of the quartz is certainly very small—indefinitely less than anything we could detect by means of the old galvanometer. The quartz rods were intended to form a complete fence round the upper plate, and practically formed a fence which was very nearly perfect, being only interrupted by gaps a few millimetres wide at the corners. The result was a slight apparent increase of resistance, but the irregularities were so great that no certain conclusion could be drawn except the following:—The conductivity observed was almost entirely, if not entirely, in the sulphur itself, and not on the surface. This was further proved by removing the drying substance (phosphorus pentoxide) and blowing in a current of warm air saturated with water vapour, when it was again noticed that no appreciable change of resistance took place. We shall see later on that the explanation of this result lies in the fact that sulphur does not appear to condense moisture so as to reduce its apparent resistance, as glass does. With the arrangement described the conductivity of the condensed layer was small compared with that of the sulphur itself. This result was true whether the quartz rods were in or out. The facts as to the conductivity of the surface of annealed sulphur were confirmed and completed at a later time.

With respect to the tests of specific inductive capacity and residual charge, we will only state that by a comparison of this film with a bit of specially-prepared mica, we observed, for the first time, that striking absence of residual effect which will be described when we deal with a film free from the objections we have raised to this one.

It now became clear that we must reduce the electric stress on the sulphur if we desired to be free from the risks of breaking the film. Consequently a number of films were prepared during February, 1891, some soluble, some a mixture of soluble and insoluble sulphur, and these were tested with lower voltages. In one case the film was cooled by carbon dioxide snow. All these films went wrong. In a very thin one the plates were found to touch at one corner. One insoluble film was dirty from having caught fire. The film cooled by carbon dioxide snow was got so cold that it became wet round the edges with condensed moisture, and some of the snow had been in contact with the sulphur, and traces of grease were suspected in the snow. One good soluble film gave no conductivity at all, but our galvanometer was not sensitive enough with the reduced voltage to make the negative result worth anything. A mixed film showed no conductivity till it was heated

nearly to melting, when it began to conduct at  $110^{\circ}$  C., and the conductivity then diminished to about  $116^{\circ}$  C., when it increased rapidly as the sulphur melted. Some films separated from the plates on heating.

The result of all this was to show us the necessity for a good many small precautions, and induce us to concentrate our efforts on the new galvanometer. This work, which has already been described, occupied us until September, 1892, when the new instrument was got into good working order and the investigation of the sulphur proceeded with. Preliminary experiments, therefore, took nearly two years, though the work was not continuous, and we blundered a good deal. With increased galvanometer sensitiveness came increased difficulty from want of insulation, thermo-electric effects, &c. These took some time and trouble to overcome, and, as our experience and the sensitiveness of the galvanometer increased, we were continually obliged to repeat our observations. The film was the subject of experiment until October 28, 1892, at which time, the plates having come apart, the thickness of the film was measured by a large spherometer. The threads having been measured before they were put between the plates, and previous work having shown that the plates rested exactly on the threads, it was imagined that the thickness of the film would be the same as the diameter of the threads. This, however, turned out to be an erroneous assumption, for the spherometer showed that the thickness varied slightly from point to point, and was more than 1 per cent. greater than the diameter of the threads. In the progress of the work it was necessary to reduce most of the results with this wrong value (*i.e.*, the supposed thickness of the film), but they have been recalculated for this paper. The exact statement of the preparation of the film follows.

*Preparation and Properties of Film of September 14, 1892.*

The plates having been scrupulously cleaned, as well as the pure gold dish, some twice distilled sulphur (Chance) was melted at a temperature of  $145^{\circ}$  in the large oil bath. This oil bath was really a large oil oven, heated by two long perforated Bunsen gas tubes. It took about four hours to heat to  $120^{\circ}$ , and was a proportionally long time in cooling; it was not the same oil bath that was used for heating the sulphur when undergoing examination. Eight threads, each broken off to a diameter of .24 millim., were placed on the lower plate. These threads were about 1 to 2 centims. long, and their diameter was gauged by a BROWN and SHARP vernier callipers. The upper plate was adjusted to the sulphur, care being taken to avoid the presence of air bubbles by lowering the plate from one end like a microscope cover-slip, and at the same time the plate was lowered gently enough not to wash out the threads. The sulphur stood in the gold dish nearly level with the top of the upper plate. After the plates were adjusted as perfectly as possible (examination afterwards showed that the adjustment was practically perfect), the whole arrange-

ment was put back into the oil bath, and again heated to  $145^{\circ}$ , after which the temperature might be considered uniform. We desired to avoid distorting the plates by having any want of uniformity in the temperature. The bath was then allowed to cool slowly to  $95^{\circ}$  C., when the sulphur crystallized, but was still soft. The temperature was then raised to  $118^{\circ}$  C., kept at this for about an hour, and the gas then turned off, and the bath allowed to cool slowly. It takes six or seven hours to reach the temperature of, say,  $30^{\circ}$  C. In order to have a check on the nature of the sulphur employed, two auxiliary aluminium plates were prepared at the same time, and furnished with a film of sulphur, under identical conditions with the actual experimental plates. The next day these plates were forced apart, and about 1 gram weight of the sulphur tested by carbon bisulphide. It was found that the sulphur was all but absolutely soluble. We would not like to say that it was not perfectly soluble, for the minute particles left could only be seen when the test-tube was in bright sunlight, and they might have been merely dust motes. However, our impression was that a trace of insoluble sulphur was present; it could not have amounted to more than about .01 milligram, so that the film may be considered to contain, say, 99,999 parts of soluble sulphur out of 100,000.

After the observations were complete, and the plates taken apart on October 25, it was found that 3 sq. millims. ought to be allowed for the space taken up by the bubbles. The film appeared to be perfectly soluble, nothing in the way of residue could be detected, but only about 1 decigram was available for testing. The melting point was taken five times, and found to be from  $120.8^{\circ}$  C. to  $121.4^{\circ}$  C., consequently the sulphur was prismatic. A microscopic investigation showed that there were larger crystals present in the film cemented together by smaller ones, or, possibly, by uncrystalline matter. We were so fortunate as to secure the assistance of an expert mineralogist, Professor DAVID, in the microscopic examination of the film. The investigation of the film at the end of the experiments, so kindly undertaken by Professor DAVID, involved grinding pieces of the film down to very fine slices, in the same manner as rock sections are ground down, and subsequent examination by the polarizing microscope. The results were as follows:—

(1.) The greater portion of the film, probably the whole, is crystalline and anisotropic.

(2.) Most of the crystals, but not all, have their principal axes lying in the plane of the film.

(3.) So far as could be seen, most of the crystals appear to have their principal axes parallel.

(4.) The question as to whether all the crystals were monoclinic was investigated with great care by observing the extinction angles, and comparing the action of the film with that of fresh and aged monoclinic crystals. The result was, that the crystals had certainly ceased to be monoclinic, and within the limit of observation were entirely octahedral. The "extinction angle" of monoclinic sulphur is at  $45^{\circ}$  to

the long axis of the crystal, in the case of the film sulphur the extinction angle had changed to about  $8^\circ$  with the original monoclinic axis. As the extinction orientation of the supposed octahedra is unknown, and the crystals are too small to observe singly, no further conclusion can be obtained.

We desire to express our thanks to Professor DAVID for the foregoing valuable addition to our knowledge of the structure of this film. It clearly consists either of a form of sulphur intermediate between monoclinic and rhombic sulphur with extinction angles of  $8^\circ$  or  $9^\circ$ , and which still preserves the melting-point of prismatic sulphur, or, on the other hand, it may perhaps turn out that the octahedra formed in this way are merely very unstable and return to the monoclinic state so rapidly that in melting-point experiments the reconversion always occurs before the melting can take place. Aged monoclinic crystals of sulphur from various sources were found to behave in the same way. Against the instability theory we have the fact that the melting-point was the same, whatever the initial temperature of the glycerine bath. During the electrical observations the film was probably partly normal monoclinic and partly "aged" monoclinic.

No quartz rods were used to reduce the surface conduction. The film was dried for some days in position in the oil bath by sulphuric acid and phosphorus pentoxide.

The colour of the sulphur was a pure lemon-yellow.

Most probable area of film,  $156.415 - .03$  sq. centims.

$$A = 156.385 \text{ sq. centims.}$$

*Thickness of Film.*—The threads were slightly conical and broken, so that the thickest parts were .024 centim. in diameter, as has been stated. When the plates were taken apart, a series of measurements of the film by the spherometer were made. Bits of the film were taken from each of the sides near the edge, and a bit from the middle. The bit to be measured was placed on the spherometer plate in a marked position—with careful dusting—and then covered by a small square of plane parallel glass, not larger than the fragment of film employed. The spherometer was well oiled and got into a steady state of temperature by handling before the zero was obtained—precautions very necessary, but generally omitted. Ten settings were taken on each portion of the film. The five means of the readings were, in inches,

.337670

.336990

.337840

.336470

.336979

---

Grand mean . . . .3371898

Zero setting on bit of glass. 10 observations, .346773.

Difference, .0095832 inch = .024341 centim. thickness of film.

The differences are probably due to imperfect dusting of the bits of film. The film was very crumbly and the broken bits were strongly electrified and difficult to remove. This measurement of film thickness is the most unsatisfactory part of the work. In calculating specific resistance and specific inductive capacity, the ratio of thickness to area has to be known.

The area has to be corrected for the effect of the edges. In the case of the electrostatic measurement, *i.e.*, the determination of the specific inductive capacity, a correction to the area can be calculated as already mentioned, and may be taken at + .26 centim. In view of the specific resistance being dependent on so many different factors, it was not worth while to try to calculate a separate correction, so that the corrected area has been used both for the calculation of specific inductive capacity and specific resistance.

This area is  $156.385 + .26$  or  $156.645$  sq. centims.

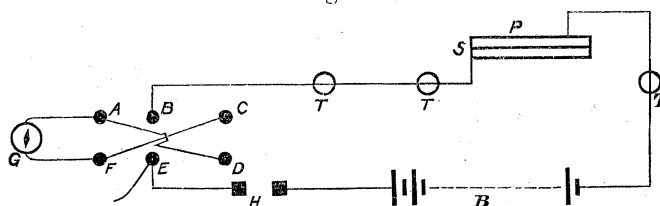
The ratio of corrected area to thickness is, therefore,

$$\frac{156.645}{.024341} = 6427.4.$$

The arrangement of apparatus adopted for making the measurement of the resistance of this film will be understood from the diagram.

Two days experimenting were absorbed in curing leaks, contact effects, &c. The galvanometer was simply used with a lamp and scale.

Fig. 1.



A B C D E F (fig. 1) is a reversing key, put to earth at E.

H is a contact key.

T, T are insulating supports of glass and ebonite.

The terminals of the battery are reversed when necessary by interchanging the wires.

A key, not shown, is provided for connecting A and F or C and D, so as to cut out the galvanometer.

Before and after making an observation the wire is disconnected from the top plate at P, and hung on the support at T. Nothing touches the upper plate except the sulphur and connecting wire. Consequently, if no deflexion occurs when the wire is disconnected from P and hung on T, even when the reversing key is put over, it shows that the insulation is sufficient.

In order to be sure that everything was in order when no deflexion was obtained on the galvanometer, the wire at P was touched with a piece of paper, which, of course, gave a deflexion, and, as additional evidence, the contact at H was broken and the sulphur plates regarded as a condenser discharged and the spark noted.

*Observation* (1).—Galvanometer sensitiveness, 1 division double deflexion for  $5.5 \times 10^{-11}$  ampère. Voltage = 313 volts.

No deflexion could be observed.

Therefore resistance of sulphur is greater than

$$\frac{313}{5.5 \times 10^{-11}} = 5.7 \times 10^{12} \text{ ohms.}$$

And the specific resistance is greater than  $3.66 \times 10^{25}$  C.G.S.

The sulphur had been exposed during two days to the action of the drying material and to the continued application of voltages of from 150 to 300 volts in both directions.

The next point was to measure the specific inductive capacity. We were delayed in this by finding, during a series of preliminary experiments, that the smaller subdivisions of a standard condenser by ELLIOTT BROS. agreed very badly, and consequently we had to make a number of comparisons in order to form an opinion as to the most reliable condenser division to use—at that time we had no condenser with standardized divisions.

Finally, we decided that the fault lay, as was to be expected, in the smaller divisions of our microfarad; we were therefore obliged to make use of the larger divisions. This necessitated the finding of a way to conveniently bridge the great difference in the capacity of the sulphur condenser and that of .2 microfarad, the smallest division available. We finally arrived at what we found to be a very satisfactory method. A preliminary experiment showed that, using a certain number of Clark cells, we obtained, by simple charge and discharge of the condenser through the galvanometer, a certain convenient deflexion. The comparison was then made by subdividing the voltage of one Clark cell and charging and discharging the selected division of the microfarad with it until a nearly equal deflexion was observed. This avoids the necessity for determining the logarithmic decrement. The voltage was divided by using points of derivation in a circuit of 100,000 ohms, including a Clark cell.

The capacity of the key and connections was found to be very nearly two hundredths (.02) of the combined capacity of the key, condenser, and connections. This correction is amply accurate enough for the results got by the ballistic method, and is rather too large—uncertainty due to large absorption in the standard prevents really good comparisons being made.

There being a difference between the divisions of the microfarad, one of them was selected as a provisional standard pending calibration when our standard shall arrive.



Let  $\theta$  be the first elongation of the galvanometer needle.

Let  $C$  be the capacity of the condenser.

Let  $V$  be the potential difference of the coatings in terms of the Clark cell.

Let  $K$  be the ballistic constant of the galvanometer.

Then when the deflexion is small and the logarithmic decrement can be neglected, or eliminated,

$$CV = K\theta; K = CV/\theta.$$

We considered that the best way of obtaining a mean value in terms of the divisions of the microfarad would be to take several sets of observations, calculate  $K$  from each and then use this mean value to enable us to find the capacity of the condenser. The results are as below.

TABLE VII.—Values of  $K$  (Galvanometer constant).

Fraction of microfarad.	Voltage.	Elongation.	$K$ .
$\cdot 2$	$\frac{1\frac{1}{2}}{5\frac{1}{2}}$ Clark	205.0	$\cdot 0002251$
$\cdot 2$		198.4	$\cdot 0002326$
Another $1/3$ standard	$1/6$ Clark	204.5	$\cdot 0002427$

Mean value of  $K = \cdot 0002335$ .

The observations on the sulphur were repeated with 21 Clark cells, as it was found that the galvanometer sensitiveness had changed since the day before, when the numbers given were obtained. In this way the mean deflexion was found to be 195.2 divisions.

Hence

$$C = \frac{K\theta}{V} = \frac{\cdot 0002335 \times 195.2}{21} = \cdot 00217 \text{ microfarad.}$$

Subtracting  $\cdot 00004$  for key and leads,

$$C = 213 \times 10^{-20} \text{ C.G.S.}$$

Corrected capacity, therefore, is  $213 \times 10^{-20}$ .

If

$A$  be the "effective area" of the film ;

$d$  „ thickness of the film ;

$\mu$  „ specific inductive capacity ;

$V$  „ ratio of the units ;

$$\mu = \frac{4\pi \cdot d \cdot C \cdot V^2}{A} ;$$

$$\begin{aligned}
 d &= \cdot 024341; \\
 A &= 156\cdot 645; \\
 C &= 213 \times 10^{-20}; \\
 V &= 3 \times 10^{10}.
 \end{aligned}$$

Hence

$$\mu = 3\cdot 748,$$

a number very like that previously obtained for the same kind of film (3·5).

Having obtained a provisional value for the specific inductive capacity of the sulphur, we considered that a suitable time had come to repeat some experiments made a year before on the residual effect, and endeavour to obtain a comparison between sulphur and mica, the latter having been much recommended by M. BOUTY ('C. R.,' vol. 110, p. 1362; 'C. R.,' vol. 112, p. 931; 'Journ. de Phys.,' vol. 9, p. 288, June, 1890; 'Ann. de Chim. et de Phys.' [6], vol. 24, p. 394). We propose to describe our experiments first, and then to discuss this very important matter (the literature of which is overwhelming) when we have described a number of cognate phenomena.

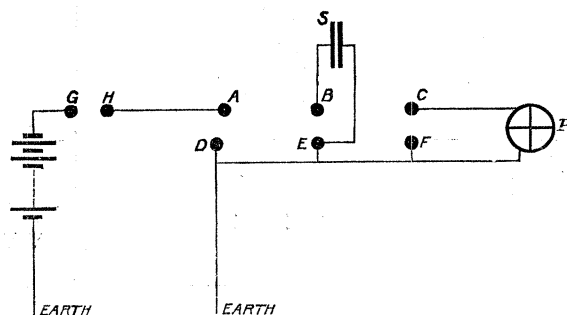
A preliminary experiment was made to find the capacity of the quadrants of our electrometer and of the key and connections used in the investigation of the residual charge. The capacity of the quadrants was rather less than ·00005 microfarad, and of the key and connections about ·000004 microfarad. The sulphur plates have, as has been shown, a capacity of about ·002 microfarad. The smallness of the capacity of the quadrants and key and leads, in comparison with the capacity of the condenser, enables us to disregard them in estimating the residual effect. The mica condenser was prepared from a specially selected bit of mica, such as is used for covering photographs; it was silvered on both sides, and cleaned along the edges as described by BOUTY, the edges being lightly varnished by dipping in a dilute filtered solution of shellac. This condenser plate was dried at the temperature of the water bath for twelve hours, and was then mounted on quartz insulators in a desiccator over sulphuric acid. It had been in this for a year when our experiments began. Connection was made to the insulated plate by means of an aluminium wire on a fused quartz support. The dimensions of the mica condenser were:—

Length of rectangular silver films . . .	7·2	centims.
Breadth . . . . .	3·6	„
Thickness of mica . . . . .	·005	centim.

The capacity was of the order of that of the sulphur condenser. We will not describe any preliminary experiments on the residual effect, because there was nothing novel either in our method or in the difficulties we encountered. The investigation of residual effect is not difficult if the effect be large, but if it be vanishingly small, as it was with the sulphur, and if it be required to assign a limit to this small effect,

then numerous difficulties arise which are to be got over by electrostatic screening, avoidance of contact forces, insulation, &c. The following diagram shows our arrangements :—

Fig. 2.



A, B, C, D, E, F (fig. 2), are the six points of a reversing key. The points B and C are insulated by supports of fused quartz. The condenser is inserted at S. GH is a pillar make-and-break key with mercury cups (see Plate 3, fig. 3). Between B and E is placed a wire of aluminium, so arranged that when the rocking key is thrown over from its charging position A B E D to its discharging position B C F E, this wire momentarily touches part of the rocker connected with B, the other end being permanently connected at E. In this way the discharge can be made to occupy a very short time, say  $\cdot 01$  sec., and includes the key. A short-circuiting key is sometimes also kept in C and F till the discharge has taken place. During the charging G and H are connected. HA is a long wire enabling the battery, &c., to be placed far enough away not to complicate matters by direct electrostatic induction. As soon as the rocker is moved over far enough to be insulated from A, this point is earthed and the rocker then moved over to CF, the short-circuiting key being removed after discharge has taken place, and, of course, before the rocker makes contact at C or F. At one time an additional key was used for the short circuiting of the electrometer, but it was given up as merely increasing the trouble of insulation. The electrometer was adjusted to a sensitiveness of about 40 scale divisions per Clark cell, and this did not vary by more than 2 divisions over the scale. Thermo-electric effects, &c., prevented the sulphur from ever giving absolutely no deflexion after the removal of the charge. About two hundred experiments were made on the sulphur and mica, and we know nothing whatever against the summary, which we consider to be a sufficient statement.

TABLE VIII.—Residual Effect in Sulphur and Mica.

Mica. Temperature 18° to 20° C.									
1. Date.	2. Number of ex- periments.	3. Voltage.	4. Charge in scale divisions.	5. Duration of charge.	6. Residual in scale divisions after 30 sec.	7. Residual in scale divisions after 1 min.	8. Percentage of charge coming out after 30 sec.	9. Percentage of charge coming out after 1 min.	10. Remarks.
Sept. 20, 1892	1	40 Clarks	1600	2 min.	12	16	.75	1	Mica heated for 38 mins. at 98° C. Not quite recovered, though it had been over P <sub>2</sub> O <sub>5</sub> all night.
"	1	"	"	3 "	12	16	.75	1	
"	1	"	"	1 "	12	17	.75	1 $\frac{1}{16}$	
"	1	"	"	2 "	12	17	.75	1 $\frac{1}{16}$	
"	1	"	"	10 sec.	11	..	.67	..	
"	2	264 volts	264 × 28	1 min.	60	..	.79	.5	
Sept. 21, "	6	318	318 × 28	1 "	40	45	.45	..	
"	4	318	318 × 28	1 "	Off scale	Off scale	..	..	
Sept. 22, "	2	> 298	> 298 × 28	1 "	300	..	< 4	..	
Sulphur. Temperature 18° to 20° C.									
Sept. 19, 1892	6	40	1600	1 min.	< 4	< 4	< .25	< .25	
Sept. 20, "	4	"	1600	2 "	< 1	< 1	< .06	< .06	
"	2	264	264 × 28	1 "	< 4	< 5	< .054	< .065	
"	"	"	"	2 sec.	< 4	< 4	< .054	< .054	
Sept. 21, "	6	> 318	> 318 × 28	1 min.	< 3	< 3	< .033	< .033	
Sept. 22, "	4	> 298	> 298 × 28	1 "	< 3	..	< .036	..	
"	2	> 298	> 298 × 28	10 "	4	< 6	< .048	< .072	
"	"	"	"	"	..	After 4 mins. was < 9, or less than .108 per cent.			
"	"	"	"	"	..				
"	"	"	"	"	..				

It will be noticed from the above that the residual charge in the case of mica—properly treated and very dry, is less by far than is generally supposed—but by exposure to air, even when heated, the effect is much increased. BOUTY's best results went to show that the residual charge was only about 1 per cent. of the initial charge; these experiments show that mica can be prepared so as to give still less. It is difficult to account for the experiment on September 21st, when the mica had been heated. BOUTY attributes the residual charge almost entirely to the action of the edges, which are varnished, and we are inclined to agree with this, but we do not see how the polarisation can be galvanic in the ordinary sense, for in our case it must have amounted to more than 10 volts. We think it is due to a creeping of the charge (see ROWLAND and NICOLL, 'Phil. Mag.' [5], vol. 2, p. 414, 1881). The sulphur is really phenomenal. We are inclined to attribute most of the small effects observed to the residual sources of uncertainty, contact action, imperfect shielding, imperfect insulation, imperfect prevention of the creeping of the charge, in spite of these effects having been eliminated apparently before the sulphur condenser was inserted. Because these uncertainties are suggested, it must not be thought that they were overlooked at the time. We believe that everything was done that could be done, and that we are, in fact, at about the limit of the applicability of these methods.

However, taking the numbers as they stand, they are sufficiently remarkable, and show that the residual charge, if it exists, is less than, say, four parts in ten thousand of the original charge, even when the duration of charge amounts to ten minutes. In our previous experiments using the film between the old gilded plates, we made use of enormously greater voltages derived from an electrophorus, but some uncertainty arose from the possible parting of the plates, and from the burning of the film where the spark had jumped across. However, we never detected any residual effect at all with the film in question, under circumstances where the residual charge from the mica amounted to more than 50 divisions; this was with a voltage estimated from the spark length at about 5000 volts.

*The electric strength of sulphur* from the broken film is in the neighbourhood of and probably greater than 730 volts per .22 millim., or at the rate of about 3300 volts per millim., or 33,000 volts per centimetre, but too much weight must not be attached to this, for the influence of a small air bubble in disturbing the field might be very considerable, and would reduce the strength very materially.

We defer the discussion of these results till the similar data for other films have been dealt with.

The residual charge having been found to be so small, rather greater interest attached to the specific inductive capacity of the film, which had to be taken again in any case in order to give us security as to the permanence of the contact between the plates and the sulphur. As the results of a complete series of very careful experiments by the ballistic method, using one division of the microfarad only, the one chosen as a provisional standard, the capacity of the sulphur was found to be—

$$C = 208 \times 10^{-20} \text{ (uncorrected).}$$

$$\mu = 3.697 \text{ (corrected for standard).}$$

A comparison between our condenser and one supplied by Messrs. CLARK, MUIRHEAD, and Co., may now be given; it was made on Jan. 24th, 1893, at a temperature of 23.8 C., by means first of the old, and afterwards of the new galvanometer, with 40 Clark cells by DE SAUTY'S method. The leakage through the two condensers was measured, and found to be so small as only to affect the result in the fifth place; it was therefore neglected. We used two 100000 ohm boxes, and a dial box of 10000 ohms, all by ELLIOTT BROS., but the divisions were not compared with our standards. Dr. MUIRHEAD'S value for the .2 microfarad was .1996 microfarad at 15° C.

As we do not know whether the mica plates are shellacked or only paraffined, we cannot apply any temperature correction—in any case the two condensers probably have about the same temperature coefficients. The result of the comparison was that with 100000 ohms out in one branch, the balance lay between 98815 and 98800 in the other. Taking 98808 as the mean, the capacity of our .2 division for instantaneous charge is .20186 microfarad, or say 1 per cent. too large. For the future this value will be employed.

The difference between this value and that formerly obtained is to be ascribed chiefly to the difference between the standard selected and the mean of the three divisions taken before as a standard.

It was thought desirable to check this result by another method, both for the purpose of obtaining independent evidence, and because the ballistic method takes so long to carry out that it is unsuited for measuring the capacity at any given temperature. The well-known method of DE SAUTY was selected after consideration, the sensitiveness of our galvanometers giving us great advantages in carrying it out. By observing the initial kick we also hoped to get the instantaneous capacity comparison (see GLAZEBROOK, 'B.A. Report,' Leeds, 1890, p. 102).

By using 40 Clark cells, a balance for instantaneous charge was given by 100000 and 1065 ohms out in the two branches, one from a dial box, the other from an ordinary box, both by ELLIOTT, but not compared with our standards.

The final corrected result is

$$C = .00211,$$

$$\mu = 3.708.$$

The sensitiveness of the galvanometer having been increased, as well as our experience in using it, it was thought worth while to determine the resistance again for the purpose of obtaining a higher limit.

*Date, October 1st, 1892—Voltage, 304 volts.*

Sensitiveness of galvanometer,  $3.6 \times 10^{-12}$  ampère per "half" tooth of the micro-meter.

Limit of certain discrimination, owing to thermal effects, was about .25 tooth only, but it is put at .5 tooth for certainty.

Specific resistance is greater than  $5 \times 10^{26}$  C.G.S. (The capacity was taken again just after the test, and found to be the same as before.)

In order to check this, it was made the subject of experiment by the electrometer method. At first we intended to experiment with different voltages in order to test the sulphur with respect to its law of conduction, and made a number of experiments on the lines of the experiments of THOMSON and NEWALL ('Proc. R.S.' vol. 42, p. 410, 1887). For reasons formerly given, however, we ended by observing the leak during a given time, and then assuming Ohm's law, we will not enlarge on our troubles in this work, for they must have been such as would come to anyone trying to get at a very high resistance by this method. We will, however, ask the reader to believe that all such sources of error as are introduced by incorrect knowledge of capacities and electrometer law—imperfect insulation, &c., were attended to by us with great care, and the results we offer are, we believe, free from objection. Mr. POLLOCK was kind enough to check the algebraical and arithmetical work for us, and as he used no approximations, we give his results rather than ours—with which they agreed within the limit of approximation adopted by us.

From the results, the specific resistance of the sulphur is as follows, neglecting fractions :—

1. Oct. 6, 1892 . *Specific Resistance*,  $6 \times 10^{28}$  C.G.S.
2. Oct. 7, 1892 . *Specific Resistance*,  $1 \times 10^{28}$  C.G.S.
3. Oct. 7, 1892 . *Specific Resistance*,  $8 \times 10^{27}$  C.G.S.

These results were obtained with a voltage of about six Clark cells.

All these observations were taken on sulphur after it had been in its silvered brass box with phosphorus pentoxide for at least twelve hours.

The effect of exposing the sulphur to air was tried on one occasion, when the resistance fell at once (*i.e.*, in ten minutes) about one thousand-fold, and seemed to stay there. After replacing the lid of the box and leaving for about twenty minutes, the resistance had again increased to six times its value when exposed freely to air. This explains partly how it was that we got only a small or negligible effect by exposing to moist air when we used the galvanometer. At the time the plates were exposed to air for ten minutes, as just recorded, the thermometer wet bulb was at  $61^{\circ}6$  F., and the dry bulb at  $71^{\circ}6$  F.—a rather damp day. Nearly all the reduction in resistance took place during the first few minutes of exposure, but the method does not admit of this matter being treated satisfactorily, for it takes too long to get a good measurement. The influence of moisture seems to be to reduce the resistance of the sulphur condenser, but not to such a point as would enable the conductivity to be detected in any measurements hitherto described by means of the galvanometer. It is possible that the small conductivity observed by the electrometer may be wholly

due to residual surface action, though later experiments lead us to think that this is not the case. The capacity test was again applied, giving the same result as before, and showing that the plates are still in position. It was decided to heat the sulphur condenser, and observe change of resistance and capacity as the temperature rose. The galvanometer was now more sensitive than before, giving one micrometer division of double elongation for  $1.31 \times 10^{-12}$  ampère. With 291 volts no effect could be detected. The result is to place the specific resistance above  $1.4 \times 10^{27}$  C.G.S. The galvanometer now approaches the electrometer in its power of discriminating small conductivities. The temperature was  $17^{\circ}2$  C.

The temperature of the bath was then raised to  $50^{\circ}$  C., at a rate of about  $2^{\circ}$  per minute, and was kept within a degree on either side for about an hour while the resistance and capacity tests were made. The capacity appeared to be exactly the same as before—*i.e.*, it did not change by as much as  $\cdot 3$  per cent., or we should have detected its variation. It will be shown later that this probably indicates an appreciable, but small, positive temperature coefficient of the specific inductive capacity. The resistance test also failed to show any signs of conduction, and the result may be considered to be the same as at  $17^{\circ}2$  C.

The temperature was then raised to  $75^{\circ}$  C., and kept there for several hours. A slight conductivity showed itself, corresponding to a deflexion of 21.3 divisions, with a voltage of about 285 volts. The specific resistance is now  $6.8 \times 10^{25}$  C.G.S. After the battery had been charging the sulphur for about an hour and a half at the temperature of  $75^{\circ}$  the deflexion fell from 21.3 to about 5 divisions, showing that the resistance had increased, say, four times by the continued application of electric stress. This being the first clear case of conductivity we had encountered, we were anxious to note any phenomenon which might present itself. The most striking effect was the discontinuity of the conduction. At first we thought that the sudden sharp kicks given every now and then by the galvanometer were due to accidental causes of some kind, but it soon became clear that the phenomenon was a real one. When the voltage is first applied the discontinuity is more marked than when it has been on for some time. In the case we have before us the galvanometer would take up a definite position of deflexion, and every two or three minutes this would suddenly increase or diminish by a large amount. The only possible way of estimating the conductivity is, therefore, to take a long series of observations and obtain a mean value, and that is what was done above. The impression forced on one while observing at the galvanometer is that a succession of irregular changes are taking place; for instance, that groups of molecules, one after the other, succumb to the electric stress, and signalise their destruction by allowing a current to pass. The conductivity in these cases, however, never falls to zero. It is, perhaps, not too much to say that all the observations are in accordance with a theory that there is a small regular and continuous conduction, superimposed on which there is something very like a disruptive conduction. We have since discovered that the discontinuous



conduction occurs also when the conduction is superficial, but that it is a real phenomenon of the conduction through sulphur as well. The temperature was constant between  $75^{\circ}5$  and  $74^{\circ}3$  C. The capacity appears to be absolutely the same as before, *i.e.*, within  $\cdot 3$  per cent.

The temperature raised to  $99^{\circ}8$ – $100^{\circ}$  C. There now appeared to be a slight fall in capacity, say  $\cdot 3$  per cent., but it was so small as to be quite uncertain.

The following resistance results were obtained :—

Double deflexion of 14.7 divisions at $108^{\circ}$ C.	Six experiments.
„ „ 22.5 „ $111^{\circ}$ C.	Four experiments.
„ „ 4.5 „ $113^{\circ}7$ C.	Six experiments.
„ „ 7.2 „ $110^{\circ}5$ C.	Five experiments.

The sensitiveness of the galvanometer had been reduced to one division for  $2.2 \times 10^{-11}$  ampère for the sake of rapidity of observation. The specific resistance (mean of above) is about  $7 \times 10^{25}$  C.G.S., but we lay no stress on it, for on applying the capacity test it was found that the plates had come apart.

The results with this film may now be summarized as follows :—

*Film of September 14, 1892.*

*Thickness*,  $\cdot 02431$  centim.

*Area* (effective),  $156.645$  square centims.

*Kind of sulphur*, either perfectly soluble, or containing less than 1 part in 100,000 insoluble.

*Crystals*, monoclinic (aged monoclinic) and octahedral. Optic axis in plane of film.

*Melting point*,  $119^{\circ}5$  C.– $120^{\circ}1$  C.

*Specific inductive capacity* at  $18^{\circ}8$  C., corrected in terms of Dr. MUIRHEAD'S standards.

*By ballistic method*, 3.697.

*By instantaneous DE SAUTY method*, 3.708. The latter value to be preferred; capacity constant up to  $100^{\circ}$  C., indicating small temperature increase of specific inductive capacity.

These values were obtained with a voltage of 40 Clark cells.

Residual charge with 300 volts, after charging one minute and discharging one minute,  $\cdot 03$  per cent., say.

Specific resistance at  $20^{\circ}$  C. by electrometer method, six Clark's, say  $1 \times 10^{28}$  C.G.S. Possibly entirely surface action. Exposed to damp air, resistance diminished in our apparatus 1000 fold.

Specific resistance by galvanometer method with a voltage of 291 volts greater than  $1.4 \times 10^{27}$  C.G.S. from  $18^{\circ}$  to  $50^{\circ}$  C. At a temperature of  $75^{\circ}$  C. the specific

resistance, after the current was on for, say, ten minutes, is  $6.8 \times 10^{25}$  C. It was probably a case of *discontinuous* conduction, and the resistance increased about four-fold during an hour's application of the voltage. The voltage was not reversed on the sulphur during these experiments, as such a course complicates matters enormously.

*Film of October 28, 1892.*

As the experiments just described broke down at a temperature of between  $70^{\circ}$  and  $100^{\circ}$  C., it was necessary to make them over again, in order to find how soluble sulphur behaves when heated up to the melting-point. For this purpose the same sulphur was re-melted at a maximum temperature of  $140^{\circ}$  C., and as there was, in our experience, absolutely no probability of our being able to anneal the film and then re-heat it to the melting-point without disturbing its contact with the plates, we decided to measure its resistance as the temperature fell. The film was prepared on October 28; it was annealed during the afternoon, and the following observations taken during the night when tram traffic was suspended and external disturbance less to be feared. The resistances were such that the old galvanometer was most conveniently employed; it was read by a lamp and scale. The temperature fell from  $140^{\circ}$  C. to  $134^{\circ}.5$  in forty minutes. The resistance was so low that only one Clark cell (the large master cell) was used. During an hour the temperature was kept between  $134^{\circ}.5$  and  $137^{\circ}.5$ , and the resistance gradually increased, so that the deflexion fell off from 396 to 354 divisions in half-an-hour. On reversing the battery at a rather lower temperature,  $132^{\circ}.85$ , the deflexion at once increased to 548, and in the course of about twenty minutes fell to 423. These results are typical. The film probably contained some insoluble sulphur at this temperature; when it was examined afterwards, several analyses showed a mean content of .35 per cent. of insoluble sulphur and a melting-point of from  $119^{\circ}.06$  to  $119^{\circ}.66$  C., but this is no criterion of the actual composition of the film at this stage. The corrected area was 156.445 square centims., and the thickness was .026188 centim. We will not trouble the reader with such a full account as in the previous case, for the procedure was exactly the same; the table will, therefore, be rather fuller. At a mean temperature of  $135^{\circ}.6$  the mean specific resistance with the battery on both ways was  $1.5 \times 10^{21}$  C.G.S., which is not much less than the resistance after an infinitely long application of voltage. The capacity at this temperature could only be taken very approximately, owing to the leak; the result was a specific inductive capacity of 5.7. We believe this is not far from the truth, but lay no stress on it.

We will give the full set of observations of resistance at the next temperature examined,  $124^{\circ}.4$  C., partly to illustrate the effect of time and reversal, and partly to enable anyone to form an opinion as to the actual effects obtained. The differences are really greater than they appear, for the ratio of two successive swings with this galvanometer was 2.507, as deduced from twelve experiments with elongations of the

same amplitude as occur in the table. The corresponding logarithmic decrement is about .4. The galvanometer sensitiveness is  $1.366 \times 10^{-11}$  ampère per scale division (ELLIOTTS, at about 1 metre) of double elongation. We have to thank Mr. POLLOCK for assistance in making all the observations with this film.

Time, 8 hours 55 minutes. Charged for three minutes, + terminal of battery to the upper plate. Voltage 1 Clark.

Temperature	123.5° C.	Galvanometer reversed	A-B.	D. deflection	338
"	"	"	"	B-A.	330
"	"	"	"	A-B.	318
"	"	"	"	B-A.	318
"	125° C.	"	"	A-B.	306
"	126° C.	"	"	B-A.	310

Time, 9 hours 14 minutes.

Battery reversed.

Temperature	126° C.	Galvanometer reversed	A-B.	D. deflection	414
"	"	"	"	B-A.	392
"	126° C.	Time 9 hrs. 20 mins.	Galv. rev. A-B.	"	392
"	"	"	"	B-A.	372
"	"	"	"	A-B.	363
"	125°	9 25	"	B-A.	348

Mean of all deflections 350.1.

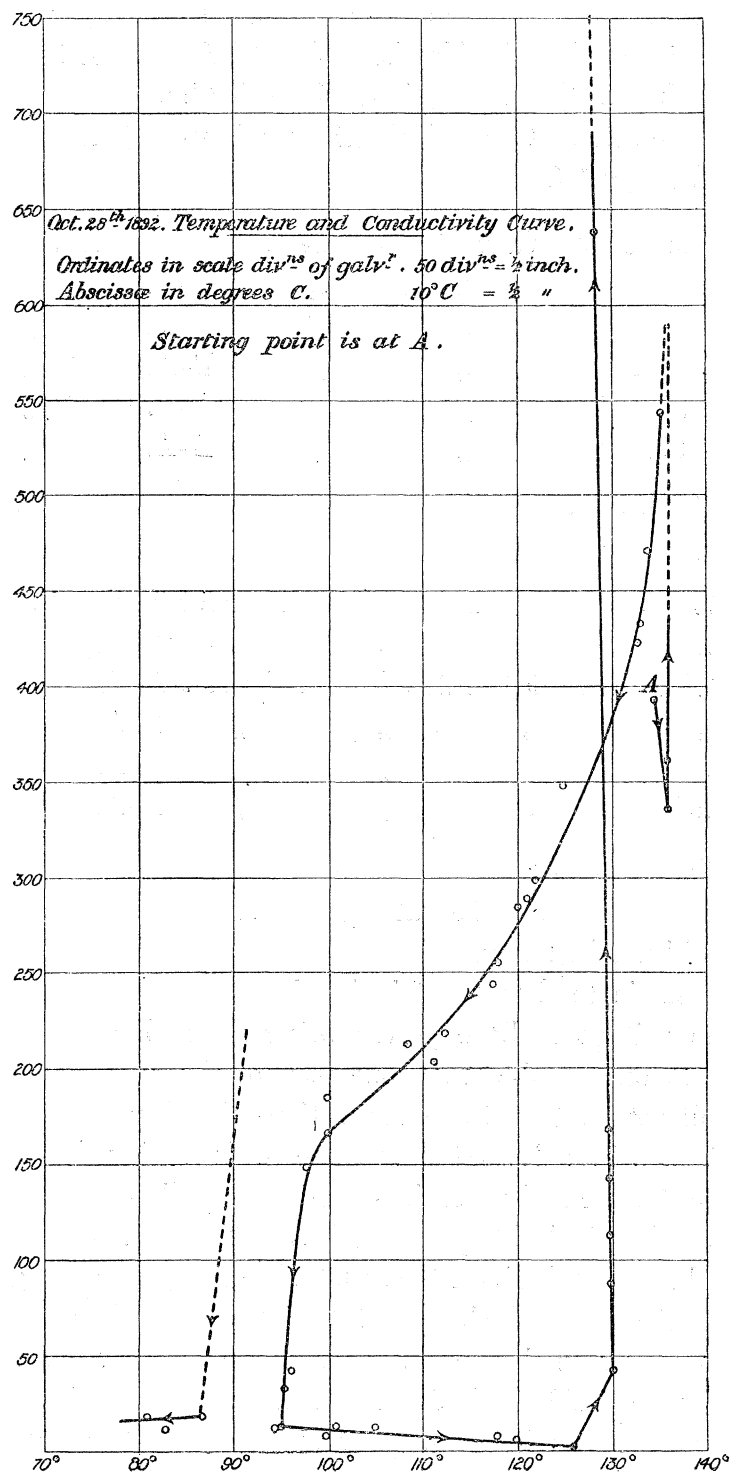
Mean Specific Resistance  $1.8 \times 10^{21}$  at say 124°·5.

The capacity could not be taken.

An attempt was made to detect residual polarization by the galvanometer—but without effect—the voltage to be expected being so small as to compare with the thermoelectric effects unavoidable with one part of the circuit so much hotter than the rest. We shall return to this. Observations showing an increasing resistance were made at various points down to 97° C., at which point the sulphur evidently began to crystallize, for the resistance increased so rapidly that we observed best by noting the rate at which the light spot moved over the scale towards the zero. The resistance increased meanwhile about twelvefold. Nothing is to be got by noting the rate of change of resistance with change of temperature, unless we had actually had a rapid thermometer between the plates. Our thermometer was merely in the inner box with the sulphur, and did not indicate the temperature-variation of the sulphur to be expected while it was freezing. The summary of the changes that occur is as follows (see table for numerical details).

- (1.) At 100° the resistance is considerably increased.
- (2.) Between 100° and 96° the rapid change begins.
- (3.) Between 96° and 93° the velocity of the change increases.

Fig. 3.



When the deflection had fallen to 12 divisions, it remained fairly constant. These results probably chiefly refer to the time of crystallization of the sulphur, which, as everyone knows (GERNEZ, *loc. cit.*), is a process requiring a good deal of time. The

sulphur was again heated and the resistance diminished steadily, till at 129·5 the spot began to move at a rate of 10 divisions per second, and went on faster and faster, till after three minutes it had gone off the scale. On cooling, the resistance was undoubtedly permanently reduced—say tenfold; it increased, as before, down to a temperature of 90° C., when the sulphur evidently crystallized and the resistance suddenly increased. A curve has been drawn (fig. 3) showing the variation of resistance with temperature, the observations being for the most part made with the voltage each way; at the points of rapid change this was not possible. The hysteresis of the diagram is partly due to the time required during crystallization. The rate of variation of temperature at important points was never more than one degree in five minutes. The permanent reduction of specific resistance by heating was observed again with another film at a later date, and appears to be a natural phenomenon.

TABLE IX.—Showing Resistance of the Film of October 28th, 1892, at Different Temperatures.

Temperatures.	Specific resistance in C.G.S. units.
135·6° C. falling . . . .	$1·5 \times 10^{21}$
124·4 " " . . . .	$1·8 \times 10^{21}$
108·5 " " . . . .	$2·9 \times 10^{21}$
100 " " . . . .	$3·733 \times 10^{21}$
96 " " . . . .	$3·3 \times 10^{22}$
95 " " . . . .	$3·5 \times 10^{22}$
101·5 " rising . . . .	$3·9 \times 10^{22}$
Above this the resistance fell as shown on the curve till about 127°, when the sulphur melted. The two following relations are taken from the curve :—	
At 128° C. rising . . . .	$9·9 \times 10^{20}$ (uncertain) change very rapid
On cooling again at 83° C. .	$3 \times 10^{22}$

\* We provisionally attribute the fall of resistance to a change in the amount of insoluble sulphur present, probably, almost certainly, an increase. It may be objected that we ought to have melted our film at a lower temperature, and thus prevented the formation of insoluble sulphur at all. The reply to this is, that unhappily one cannot adjust the plates properly unless one has some time for the operation, and the cooling surface of the plates is so great that sufficient time is not afforded if the sulphur is nearer to its crystallizing point to begin with.

*Film of November 9th, 1892.*

It was now necessary to examine the behaviour of a film rapidly cooled so as to form a mixture of soluble and insoluble sulphur. Our first attempt failed, owing to

\* Further research shows that this provisional conclusion must be modified.

water getting on the film, the second attempt succeeded. The sulphur was heated to a temperature of about to  $250^{\circ}$  C., and kept there for fifteen minutes; the cooling was effected as rapidly as possible by water, consistently with not allowing any water to touch the sulphur. Some portions of the sulphur were cooled more rapidly than others, and consequently the percentage of insoluble sulphur present varied in samples taken from different parts of the dish. The film itself probably contained about 5.2 per cent. of insoluble sulphur, but this estimate is based on analysis of sulphur cut away from the sides of the plates close to the film. The film itself was heated in the course of the experimental work, which rendered any conclusion from the analysis in its final state inapplicable.

The melting-point of the sulphur, after it had been between the plates as the subject of experiment, was from  $119.31^{\circ}$  to  $119.86^{\circ}$  C.

The area of the film (corrected for bubbles, &c.) was 155.845 sq. centims.; the thickness of the film, by spherometer, was .02718 centim.

As the specific inductive capacity appeared very different in this case from the values found previously for soluble sulphur, and as the thickness of the film is the most critical measurement in determining the value, we will give the means of four groups of ten settings, each on pieces taken from different parts of the film from which the thickness was deduced. They are

Setting.	Thickness in inches.
(1) .336764	.009947
(2) .334774	.011937
(3) .336211	.010500
(4) .336190	.010521

Mean, .335985 inch.

Ten settings on glass. Mean, .346711.

Difference, .010726 inch = .02718 centim.

We consider that the greatest possible error of any group of settings cannot amount to more than 4 per cent., or the film is clearly not quite regular.

A measurement made by focussing with a Zeiss microscope gave about .03 centim., but it is only of value as a rough check. It will be safe to consider the mean thickness as correct, within, say, 10 per cent., at least.

The sulphur (as soon as the plates were sufficiently cooled by placing the outer dish in water and putting wet filter paper on the upper plate) was set up in the oil bath with drying material. A rough test at a temperature of  $22.8^{\circ}$  C., voltage 265.3, made with the old galvanometer, gave—

Specific resistance,  $4.2 \times 10^{21}$  C.G.S.

No marked difference was observed between the conductivity when the battery was first on, and five minutes afterwards, but the resistance slowly increased as usual.

The capacity was measured by the DE SAUTY method, using the small storage cells with a voltage of 265.3 volts. The instantaneous balance was reached with between 1070 and 1072 out in one arm, and 100,000 out in the other. The resulting capacity was  $.002142 \times 10^{-15}$  C.G.S. Applying a correction of  $-2$  per cent. for the key and  $+1$  per cent. for the value of the standard, or, in all,  $-1$  per cent., this becomes .00212, say. The corrected value of the specific inductive capacity is 4.1814. We can only explain this large value by supposing that the film measurement is at fault, or that the specific inductive capacity of mixed sulphur is really high. The film measurements are given in order to allow the reader to form his own opinion on this point.

The sulphur was kept in the drying box for 24 hours at a temperature of about  $22^{\circ}$  C. The specific resistance  $= 5.05 \times 10^{24}$  C.G.S.

So it has not changed much by continued drying; the battery was not reversed, and the mean deflection was 57 divisions. After the battery had been applied for about one hour the double deflection fell to 17 divisions. The voltage was 264 volts. The current having become fairly constant, it was thought advisable to investigate whether the deflection was due to surface conductivity. From previous experiments it is known that the sulphur surface conductivity, after a day's drying, will not make the apparent specific resistance less than of the order of  $10^{27}$  C.G.S., but this was with highly soluble sulphur. It is not likely that the admixture of insoluble sulphur will increase the surface conductivity, but it is possible that it may do so, and in that case we should expect that exposure to damp air would reduce the apparent resistance. The lid was therefore taken off the thermostat, and the plates freely exposed to the air for ten minutes. Dry bulb,  $72^{\circ}$  F.; wet bulb,  $65.5^{\circ}$  F. No change having been detected, a current of air which had been passed through a reversed wash-bottle with the water at  $50^{\circ}$  C., was allowed to play for about five minutes on the sulphur between the upper plate and the dish. The deflexion or reversal of the galvanometer remained precisely the same as before. The conclusion is that the conductivity is probably almost wholly due to the sulphur, and that the latter is not affected by damp air to anything like the same extent as glass is. This is confirmed by some observations to be described, in which, when the sulphur plates are heated in a closed box with drying material to  $50^{\circ}$  C., the conductivity is increased, whereas, if it were due to surface action, the opposite effect would be expected. The sensitiveness of the galvanometer (new), when these experiments were made, was about  $5.2 \times 10^{-12}$  ampère per micrometer scale division, and the period was eleven seconds. This (November 10, 1892) was the steadiest day we ever had, the galvanometer could have been read to .2 division perfectly, had it been necessary. The next day was almost equally steady, and we had a good example of the effect of variable con-

ductivity, which was further shown by the galvanometer needle kicking slightly from time to time. The following table will indicate the effect we mean; we often observed it, but on this occasion the magnetic conditions were so steady that we are able to be quite certain that the effect is not to be explained by accidental irregularity. When taking the sensitiveness of the instrument, within a few minutes, not a trace of such an effect was to be observed, and the insulation of the wire, &c., was found to be perfect, as far as our methods would show.

TABLE showing Irregular Conductivity of Sulphur Film containing a Mixture of Soluble and Insoluble Sulphur.

*Date*, Nov. 11, 1892. *Voltage*, 268·4.

*Sensitiveness*,  $5·43 \times 10^{12}$  ampères.

*Temperature of air*, 19°·9 C.—*of sulphur*, 20°·3 C.

After the voltage has been applied long enough for the sulphur to take up a steady state (say 20 minutes)

A-B, double elongation, 6 divisions.

B-A,	„	„	18	„
A-B,	„	„	6	„
B-A,	„	„	6	„
A-B,	„	„	6	„
B-A,	„	„	16	„
A-B,	„	„	33	„
B-A,	„	„	29	„

The capacity was found to be exactly the same as before, and the plates regarded as a condenser gave a bright spark on discharge.

This irregular conduction (though not always so well-marked) was generally observed, and may be considered as a natural phenomenon.

The sulphur was then tested for residual charge in the manner formerly described. Sensitiveness of electrometer was 41 divisions per Clark cell: the insulation of all the apparatus was so good that no corrections had to be applied for leakage. After charging for five minutes with a voltage of 238·6 volts, the residual charge gave a deflection of 9·5 divisions in one minute, and 11 divisions after two or three minutes more. If we take 10 divisions as a basis of calculation, the residual charge is ·147 per cent. of the initial charge, or between three and four times as much as we got before. But the conductivity is, say, a thousand times greater, which seems to show that there is no accounting for the residual effect by considering the conductivity alone. If we adopt MAXWELL'S calculation as a basis, then the variation

$\frac{\text{Specific Resistance}}{\text{Specific Inductive Resistance}}$  from layer to layer is greater in the case under consideration than in that formerly dealt with. The conductivity of the film was not great



enough as a whole to account for any serious diminution of the residual charge, as was ascertained by observing how the residual charge was held. The voltage of the residual charge was only about .3 volt in this case, and less in the former case—so that it is conceivably a case of galvanic polarization only. Against this, it may be urged that the residual charge increases with the time—strong evidence that the polarization is dielectric, not galvanic. In order further to test this conclusion 103 volts, instead of 238.6, was applied for the same time (five minutes), and the residual charge, after one minute, was found to be .187 per cent. of the initial charge. A good many very concordant observations were used in obtaining these values, and there is no doubt about the residue being larger in proportion with the smaller voltage. This result is not in accordance with the results obtained by BOUTY for mica condensers, which was, at all events, partly owing to the charge creeping over the mica edges. In our case, we cannot assert that the small residual charge observed by us was not due to the charge creeping over the sulphur surface. Since the residual is so small that we are unable to discover its origin by experiment, there is not much to be gained by speculation. We may, however, say that this film was probably a great deal more wanting in homogeneity than the perfectly soluble film, and that we expected a much larger residual charge in consequence. That such was not obtained, may either indicate that the possible explanation suggested by MAXWELL does not apply in this case, and that we are actually in presence of the new kind of polarization he suggests, or that though the want of homogeneity is considerable, the variation of the ratio of specific inductive capacity to specific resistance, from point to point, is only small.

As there is every reason to expect that the constitution of a mixed film will continually change, owing to instability of the insoluble sulphur and the gradual tendency of monoclinic to pass into octahedral sulphur, the capacity was taken again in order to detect any change that might have taken place. This was seven days after the film was first made.

The capacity of the condenser was found to have changed somewhat, more than the change of temperature would be likely to account for, temperature  $21^{\circ}5$  for both condensers, corresponding to a change of only  $.3^{\circ}$  C. The capacity now was such that the balance changed from 1071 to between 1089 and 1090 with 40 Clark cells. This leads to a value of  $K$  of 4.247 as against 4.1814 obtained before. There is no doubt about the film having undergone some change. The resistance was, therefore, measured (battery both ways) and found to be  $5.018 \times 10^{25}$  C.G.S., with a voltage of 262.8 volts and a galvanometer sensitiveness of  $4.9 \times 10^{-12}$  ampère per micrometer division. The resistance has, therefore, increased also. There is no doubt that a real change has taken place, for the increase of specific inductive capacity precludes the possibility of the plates having separated. We attribute this to the conversion of the prismatic sulphur into octahedral, the only change to be expected, so that the specific inductive capacity is higher for the latter than the former. The film was

then heated and observations made at from  $60^{\circ}$  to  $64^{\circ}$  C. The resistance was found to have diminished, the conduction was unsteady and the usual effects were observed. With battery both ways after the steady state was reached the conduction was found to have increased between  $60^{\circ}$  and  $64^{\circ}\cdot8$  in the ratio of 44·2 to 31·2 (the respective elongations deduced from 24 observations). The value of the resistance at  $64^{\circ}\cdot8$  C. is  $6\cdot9 \times 10^{24}$  C.G.S. The value of the specific inductive capacity at  $67^{\circ}$  C. was apparently 4·25, and at  $98\cdot5$  could not be distinguished from this; the temperature of the standard did not change meanwhile. At  $100^{\circ}$  C. the resistance was much decreased and the conduction unsteady, the effect on reversal was not so strongly marked. Thus :

Temperature,  $100^{\circ}\cdot5$  C.

*Battery A.*

Double elongation . . . . .	472
Ditto, reversed . . . . .	465

*Battery B.*

Double elongation (at once) . . . . .	444
Ditto, reversed . . . . .	465

The results of these experiments are collected in the following tables :—

TABLE X.—Showing Variation of Specific Inductive Capacity of Film of  
November 9, 1892.

Date.	K.	Temperature of sulphur.	Temperature of standard and resistances.	Voltage.
1892.		$^{\circ}$ C.	$^{\circ}$ C.	
Nov. 9 . . .	4·18	22·8	22·8	40 Clark's
" 11 . . .	4·18	19·9	20·3	"
" 16 . . .	4·247	21·5	21·5	"
" 17 . . .	4·247	67·5	21·4	40 Clark's and 262 volts.
" 17 . . .	4·247	98·5	21·15	" " "

In the above table no corrections are applied for increase in the linear dimensions of the electrodes. If this be done it will be found that the constancy of the capacity as the temperature rises indicates a small positive temperature coefficient in the specific inductive capacity which may, however, be due to a partial annealing. This is dealt with later when we had command of a better standard.

TABLE XI.—Resistance of Film of Mixed Sulphur of November 9th, 1892.

Date.	Voltage.	Resistance.	Specific resistance.	Temperature of sulphur.	Temperature of air.	Remarks.
1892.	volts.	ohms.	C.G.S.	° C.	° C.	
Nov. 9	265.3	$7.358 \times 10^{11}$	$4.178 \times 10^{24}$	22.8	22.8	Directly after cooling
" 9	"	Half of above	Half of above	"	"	In fifteen minutes
" 10	264.1	$8.9 \times 10^{11}$	$5.5 \times 10^{24}$	22.6	"	After voltage had been applied for half-an-hour. The resistance was not affected by blowing in damp air
" 11	268.4	$3.296 \times 10^{12}$	$1.87 \times 10^{25}$	19.9	20.3	Discontinuous conduction.
" 17	262.8	$8.75 \times 10^{12}$	$5.02 \times 10^{25}$	21.4	20.5	Battery only one way
" 17	"	$1.2115 \times 10^{12}$	$6.88 \times 10^{24}$	64.8	"	Battery both ways
" 17	"	$4.945 \times 10^{10}$	$2.836 \times 10^{23}$	100.5	"	Ten observations. Battery both ways

The resistance results may be summed up as follows :—

(1.) The mixed sulphur film is at least 1000 times more conducting than the purely crystalline film.

(2.) The resistance changes from day to day, independently of the surface action, and is always less (*a*) when the voltage is first applied, (*b*) when it is reversed (at ordinary temperature).

(3.) The resistance is discontinuous, particularly when the battery is first applied.

(4.) The resistance decreases nearly two hundredfold between 28° and 100° C.

(5.) Dampness cannot increase the surface action beyond a certain point; thus with our arrangement it could not bring the apparent specific resistance down below  $10^{23}$  C.G.S.

*Film of November 18th, 1892.*

An attempt was made to increase the amount of insoluble sulphur present by cooling the plates more rapidly. With this object in view the sulphur and plates were heated up to 260° C., and kept at that temperature for half-an-hour. During the heating (which was carried out in an improvised air bath) a stream of pure carbon dioxide, dried by calcium chloride only, was allowed to flow into the air bath. In spite of this some of the sulphur caught fire. The plates were cooled by placing the dish on a block of ice, and covering the upper plate with a zinc tray filled with ice. By this means the metal plates, and with them the sulphur, were reduced to a temperature of nearly 0° C. in less than five minutes. The cooling at the commencement was very rapid, and no water got on to the film or into any part of the apparatus. Several analyses were made of the material from the dish, but they varied between 5 per cent. and 7 per cent. only; rather to our surprise. We believe,

however, that the film was more quickly cooled than the sulphur round its edges, in which case the film probably contained upwards of 7 per cent. of insoluble sulphur. The colour of the sulphur in the dish was anything but satisfactory—it was appreciably darker than it ought to have been—especially immediately after cooling. Some samples were cut out with difficulty from round the plates, and on evaporation from platinum left an appreciable stain.

It was thought that possibly the carbon dioxide atmosphere in which the sulphur was heated had led to contamination under the action of the slightly burning sulphur. A number of experiments were therefore made by setting fire to sulphur in partial carbonic acid atmospheres, but no trace of contamination could thus be brought about. We consider the dark colour as probably due to the action of a certain amount of dust which must have collected on the sulphur during the manipulations—some of the same sulphur having been used in a previous experiment.

The results obtained with this film were similar to those with the last film, but with the peculiarities exaggerated. The plates were ultimately caused to come apart by raising the temperature, and it was then found that though the film was not as strongly coloured as the sulphur round the edges, it was distinctly darker than it ought to have been. It was much broken up by air bubbles, and not at all regular in thickness. The upper plate was slightly displaced. The mean corrected area may be taken at 155 sq. centims. The mean thickness at .021405 centim.\*

The melting-point of the sulphur was taken as usual in several experiments in which the temperature of the bath before the sulphur was introduced was gradually raised to within a fraction of a degree of the melting-point, so as to avoid annealing. The constancy of the results showed that this was satisfactorily attained. The sulphur used to find the melting-point was cut from the sides of the plates as close as possible to them. The temperature at which melting commenced was  $116.86$ ; it was complete at  $118.193$ . The initial temperature of the bath varied from  $111.46^{\circ}$  to  $117.26^{\circ}$ . The capacity taken when the film was first dried in the thermostat, gave a corrected value for the specific inductive capacity of the sulphur of about 4.404. The resistance was tested after drying with phosphorus pentoxide for 20 minutes, and after charging with 258 volts for five minutes. The deflection of the galvanometer was about 75 divisions; on reversing the battery and placing the galvanometer in circuit, after about two minutes, the deflection on reversal was too great to observe, but was estimated at about 270 divisions. After keeping the battery on this way for 15 minutes, and again reversing the galvanometer, the deflection amounted to 126 divisions. After

\* A subsequent examination of the measurements showed great differences between the thickness in different parts of the film, and the plates were afterwards discovered to have lost their perfect flatness. The absolute values, both of the specific resistance and specific inductive capacity of this film, cannot, therefore, be completely relied upon. It is probable that the value of  $K$  is too small, and  $\rho$  too large, from the uncertainty mentioned.

10 minutes the battery was again reversed, and the deflection could now be read. Successive elongations on reversal of the galvanometer were

252, 153, 153, 135, 108, 135,

and as before the conduction was discontinuous, the galvanometer needle being thrown violently in the direction of increased conduction every few minutes, and then coming quickly back. The mean effect both ways reduced to a specific resistance of  $2 \times 10^{12}$ . The film was then left for six days in the box with the phosphorus pentoxide, so as to get thoroughly dry, in case it was not so when the above results were obtained.

The effect of time on the resistance was noted as follows:—

*Temperature of sulphur*,  $23.8^{\circ}$  C. *Voltage*, 312 volts.

On first applying the voltage + of battery to insulated plate the deflection corresponded to a resistance of  $2 \times 10^{12}$  ohms.

After three minutes this increased to  $2.6 \times 10^{12}$  ohms ;

After twenty-five minutes to  $3 \times 10^{12}$  ohms.

The battery was then reversed, the initial effect died out in about three minutes, and during ten minutes' observations were made so as to fix a mean value for the resistance, with the previous observations.

Up to three minutes the resistance was  $2.8 \times 10^{12}$  ohms.

From three to ten minutes mean resistance was  $4.41 \times 10^{12}$  ohms.

It is not easy to get very accurate values, because the change is always going on, and the discontinuous conduction makes it necessary to have several observations at each point.

To test whether OHM's law was obeyed, we applied a voltage of 155 volts, and took the resistance both ways, up to three minutes, reversing several times first. The mean value was  $R = 4.69 \times 10^{12}$ , instead of  $2.6 \times 10^{12}$ , when we used the higher voltage. This result was probably affected both by the fact that the large voltage was applied first, and by the influence of the time action, though the latter was eliminated so far as possible. We do not think that the deviation from OHM's law observed can be explained away by any of these effects. A substance, whose conductivity may be a function of the quantity of electricity which has passed through it, can hardly be expected to obey OHM's law.

On November 29, after the sulphur had been allowed to rest, the resistance was found, by reversing the battery (312 volts), and allowing the voltage to remain on for three minutes each way. The two sets of deflections were nearly equal, showing that a steady state had been reached. The resulting value was

$$\text{Resistance} = 3.6 \times 10^{12} \text{ ohms.}$$

After one hour and twenty minutes this increased (with battery on one way only) to

$$R. = 1.06 \times 10^{13}.$$

Half the battery (158 volts) was then applied the same way, and the resulting value was

$$R. = 1.5 \times 10^{13},$$

or OHM's law is not obeyed, though the steady state has been reached.

The battery having been on one way for about two hours, it was thought a good opportunity for us to measure the effect of reversal, but, on this being done, the conduction was too great to be observed for several minutes; after, say, five minutes, it was still six times greater than before the battery was reversed. The full voltage was employed, and the resistance went on increasing, the current falling towards its former value for ten minutes, when observation had to be suspended.

The effect of keeping the sulphur exposed to the action of the battery seemed so definite, and at the same time so curious, that it was thought worth while repeating the observations. This was done on December 1, 1892, at a temperature of  $23.6^{\circ}$  C., and a voltage of 288.6 volts. After a preliminary test, to see that all was right, the positive end of the battery was put to the top sulphur plate and left, thus connected for one hour; there was then a mean throw on reversal through the galvanometer of 28 divisions; the current had become practically constant; the observations were:—

Throw A — B . . . . .	30 divisions
„ B — A . . . . .	27 „
„ A — B . . . . .	30 „
„ B — A . . . . .	25 „

The telegraph pole in circuit only gave an elongation of 2 divisions. The mean elongation due to current through the sulphur is therefore 26 divisions. On reversing the battery, and observing, as quickly as possible—within about two minutes—the first two elongations were in the mean 92 divisions; after five minutes (about) this fell to 71 divisions; after thirty minutes to 27 divisions. On being again reversed, the first elongations were 81 divisions; after six minutes 75; and after thirty minutes 26 divisions. On again reversing the first effect was only 43 divisions, so that the sulphur behaves as if it got fatigued, and refused after a time to show the effect. If we suppose that the conduction is the expression of the breaking-up and re-arrangement of molecular groupings, such change being from more complex to more simple, this is the effect we should expect when the groups capable of giving way under the applied electric stress became weeded out.

In these experiments of December 1 the smallest specific resistance observed was  $2.1075 \times 10^{25}$  C.G.S., and the greatest  $6.079 \times 10^{25}$ .

The galvanometer sensitiveness was  $1.32 \times 10^{-12}$  ampère per micrometer division of double elongation.

*Effect of rise of Temperature, December 2nd, 1892.*—Temperature of sulphur,  $21.1^{\circ}$  C. Normal resistance (*i.e.*, after three minutes charging each way) was

$4.942 \times 10^{12}$  ohms, and the corresponding specific resistance was  $3.578 \times 10^{25}$  C.G.S. Voltage, 305 volts. The temperature was raised slowly to  $96^\circ$  C. and kept constant at this temperature. The resistance decreased very rapidly, and was observed to be  $R = 3.198 \times 10^{10}$  ( $\rho = 2.315 \times 10^{23}$ ) before the spot went off the scale and the voltage had to be reduced. This is a reduction of, say, one hundred and sixty fold. The behaviour of the film was now curious. The temperature being allowed to rise from  $96^\circ$  C. to  $100^\circ$  C. in thirty minutes, the conductivity went on increasing so fast that the battery voltage required to be continually reduced at  $100^\circ$ , and after thirty minutes the conductivity had increased to one hundred times (say) its value at  $96^\circ$ . This increase of conductivity did not take place gradually, but by jumps—the galvanometer needle was thrown further and further out by sharp jerks which continually tailed off only to recommence. This effect went on till the temperature of  $102^\circ$  C. was reached, in fifteen minutes, after this the temperature was allowed to fall in order to discover whether the change in the sulphur would reverse. This it did immediately—the light spot coming back as markedly as it had previously moved off. An attempt was then made to reverse the change again, and the temperature was slowly raised to  $105^\circ$ , but the resistance still went on increasing. This suggested that the plates were coming apart, and on examination when all was cold this was found to be the case, for, though no sign of cracking was to be seen, the capacity was found to vary when a tinfoil coated jar placed on the upper plate was filled with about 50 lbs. of mercury. The plates were therefore dismounted, and the upper one was found to be only held in position by the sulphur round its edges. We were pleased to find the capacity test so sensitive and positive. We looked carefully too see if there was any indication of a spark having passed, but could find no reason for supposing that this had taken place; we do not think we could have missed it if such had been the case.

The following table will sum up the resistance results.

TABLE XII.—Showing Resistance of a Film containing 7 per cent. (?) of Insoluble Sulphur.

Date.	Temperature of sulphur.	Temperature of air.	Voltage in volts.	Specific resistance.	Remarks.
1892. Nov. 18	° C. 22.8	° C. 22.8	258	$1.905 \times 10^{24}$	Taken immediately film was supposed to be dry
„ 25	22.7	23.8	312	$1.47 \times 10^{25}$	First application of voltage. Battery not reversed
„ 25	„	„	„	$1.85 \times 10^{25}$	After about 3 minutes. Battery not reversed
„ 25	„	„	„	$2.18 \times 10^{25}$	After 25 minutes. Battery not reversed
„ 25	„	„	„	$2.05 \times 10^{25}$	Mean resistance battery both ways—after 3 minutes
„ 25	„	„	155	$3.4 \times 10^{25}$	Battery both ways—after say 10 minutes
„ 29	23.5	24.5	311.7	$2.61 \times 10^{25}$	Mean after 4 minutes. Battery both ways
„ 29	„	„	„	$7.7 \times 10^{25}$	After charging one way for 1 hour 20 minutes
„ 29	„	„	154	$1.068 \times 10^{26}$	After charging one way to test for Ohm's law in steady state
Dec. 1	23.6	22	288.6	$2.1 \times 10^{25}$	Least resistance obtainable on reversal after 30 minutes charge
„ 1	„	„	„	$6.079 \times 10^{25}$	Greatest resistance obtainable, battery one way for 30 minute charge
„ 2	21.1	20.6	304.9	$3.578 \times 10^{25}$	Mean resistance both ways after 3 minutes
„ 2	97	„	„	$2.3 \times 10^{23}$	After very slow heating—battery only applied at this temperature
„ 2	100	„	..	..	Resistance decreasing so fast as to be immeasurable, at most specific resistance about $2 \times 10^{21}$

*Film of April 17th, 1893.*

It has been already stated that some uncertainty attached to the constitution of the film just considered, and this was increased when, on examining the electrodes by the true plane, it was found that one of them had not preserved its perfect flatness. Another circumstance conspired to induce us to re-examine mixed films. For this purpose the plates were again adjusted for flatness, and a proper zinc dish constructed to carry ice on the upper plate. In order to obtain further security against surface action we reverted to our old plan of erecting a quartz rod fence along the sulphur surface between the dish and the upper plate. The sulphur employed was some of



the Chance sulphur given to us by Mr. CHANCE. This was melted and strained\* to get rid of particles of dirt, and was then twice distilled.

With this sulphur we made a film on April 17th, 1893, and put it in the box while still warm with phosphorus pentoxide and sulphuric acid.

The data are—corrected area, 156.64 sq. centims. (including edge correction); thickness, .022686 centim.

It consisted of soluble prismatic sulphur (probably without admixture of octahedral sulphur), with 5 per cent. of insoluble sulphur. Colour, clear lemon-yellow. When the plates were separated the greater part of the film was still transparent, but it became opaque on rubbing or attempting to detach it from the plates. We think it probable that since the film was much broken and torn up in forcing the plates apart, that it was in the transparent form during the experiments, at all events before it was heated. In this case, it must be considered to have consisted entirely of monoclinic and amorphous sulphur.

An elaborate investigation of the properties was made but, as nothing new turned up, the table will afford sufficient information. The resistance is uniformly higher than in the case of the film of similar composition of November 9th, 1892. We attribute this to the fact that, having now a great deal more material, we probably succeeded with the purification rather better than before. Of course the test of burning two hundred grammes weight was carried out, and resulted in such an almost inappreciable residue that we must have succeeded better than was to be expected in keeping the dust off during the burning, or rather boiling.

\* Sulphur is conveniently filtered by means of glass wool in a zinc funnel. A bit of platinum wire gauze, folded several times, should be placed below the funnel to catch any shreds of glass that may come through. This precaution is very necessary. Chance sulphur treated like this has a horrible smell of gas-lime when it is broken up after cooling, which shows that it requires to be distilled if sure results are to be obtained.

TABLE XIII.—Film of April 18, 1893.

The Film was composed of a mixture of 95 per cent. soluble prismatic sulphur with 5 per cent. Insoluble Amorphous Sulphur.  
Area of film, 156.64 sq. centims. Thickness of film, .02268 centim.

Date.	Voltage.	Galvanometer sensitiveness. In amperes per scale division of a double deflexion.	Direction of voltage.	Duration of voltage.	Resistance.	Specific resist- ance.	Temperature in centi- grade.	Double deflexion.	Remarks.
1893. Apr. 19	280	$4.95 \times 10^{-12}$	+ to top	23 hours	Greater than $1.12 \times 10^{23}$	Greater than $7.7 \times 10^{26}$	19.5	.5	The quartz-fence was in position. The plates had been drying for 24 hours by $P_2O_5$
" 19	"	"	—	5 minutes	$7 \times 10^{21}$ C.G.S.	$4.8 \times 10^{25}$	"	4	Taken as soon after reversal as convenient
" 24	"	"	+ and —	3 "	$5.6 \times 10^{22}$	$3.9 \times 10^{26}$	18.5	1	After drying for four days. Not changed by removing quartz, exposing to air for 10 minutes, and breathing on. Wet bulb thermometer stood at 60° F.; dry bulb thermometer at 65° F.
" 24	6 Clark's	By electrometer method for leakage in 30 minutes			$7.36 \times 10^{22}$	$5.08 \times 10^{26}$	"	..	The quartz was not replaced. This is to be compared with the other experiment of the same date
" 26	280	$4.95 \times 10^{-12}$	+ and —	5 minutes	$5.6 \times 10^{22}$	$3.9 \times 10^{26}$	31	1	Conduction steady up to 33° C. Quartz not replaced
" 26	"	"	"	"	"	"	45	"	Conductivity remains about the same up about 45°
" 26	"	"	"	"	$1.9 \times 10^{22}$	$1.3 \times 10^{26}$	53	3	Considerable discontinuous con- duction. Influence of time well marked
" 26	"	"	"	"	$1.1 \times 10^{22}$	$7.8 \times 10^{25}$	63	5	Ditto
" 26	"	"	"	"	$5.6 \times 10^{21}$	$3.9 \times 10^{25}$	68	10	Ditto
" 26	"	"	"	"	$1.1 \times 10^{21}$	$7.8 \times 10^{24}$	71	About 50	Considerable conduction increases rapidly. Influence of time well marked
" 26	"	"	"	"	$7 \times 10^{20}$	$5 \times 10^{24}$	80	80	Quartz replaced. Has no effect. Conduction increases rapidly

TABLE XIV.—Film of April 18, 1893 (continued).

Date.	Voltage.	Galvanometer sensitiveness. In amperes per scale division of a double deflexion.	Direction of voltage.	Duration of voltage.	Resistance.	Specific resistance.	Temperature in centigrade.	Double deflexion.	Remarks.
1893. Apr. 26	280	$4.95 \times 10^{-12}$	+ and —	5 minutes	$5.6 \times 10^{30}$	$3.9 \times 10^{24}$	81°	— 100	See special table for details of the rapid rise in conduction and the lag of resistance on cooling. So that in spite of the quartz the sulphur has had its conductivity slightly increased by the heating. See tables
" 27	315	"	"	"	Say $7.7 \times 10^{31}$	Say $5.3 \times 10^{25}$	18.8	Say 4	

## DETERMINATION OF K.

Comparison of Sulphur Condenser with .1 microfarad division of a mica standard. All corrections made.

Date.	Voltage.	Galvanometer sensitiveness.	Resistance out in one arm.	Resistance out in other arm.	Capacity.	Temperature.	K.	Temperature coefficient.	Remarks.
1893. Apr. 20	40 Clark's	$4.95 \times 10^{-12}$	$10^5$	2463 ohms	$2.463 \times 10^{-21}$	19.5° C. (both)	4.482	..	Balance correct to less than 1 ohm in smaller arm
" 26	"	"	"	"	"	71.3 C.	4.4824	$1.9 \times 10^{-6}$	Ditto

The question of surface conductivity is finally settled by this film ; we got just the same results whether the quartz rods were in or not, or whether we kept the film in the box or exposed it to damp air, or even breathed on the surface of the sulphur between the dish and the upper plate. Using the excellent condenser of Messrs. CLARK, MUIRHEAD, and Co., we were enabled to make the capacity comparisons with greater accuracy, and are thus in a position to assign an approximate value to the temperature coefficient of the specific inductive capacity—which turns out to be positive, and of the approximate value  $1.9 \times 10^{-6}$  per degree Centigrade.

The increase in specific resistance suggests that perhaps even now we are not using a material of sufficient purity. In favour of this view we may state that the film was not quite evenly coloured, some portions appearing of a browner shade than others. On the other hand we know of no reason to suspect any impurity, even the action of dust having been carefully guarded against, and the sulphur itself being admirably pure. It was perhaps, however, insufficiently exhausted of gas. On the other hand, we know that when annealed the resistance of sulphur as we used it is much higher, and it is difficult to credit a supposed impurity with the property of itself undergoing a change of constitution at the same temperature as that at which sulphur anneals. The observations show a very definite reduction of resistance as following a rise of temperature to  $80^{\circ}$  C., and this persists to some extent on cooling. We noticed this before. We know from a special experiment, in which some finely-powdered sulphur was heated to  $80^{\circ}$  C. for an hour, that the percentage content of insoluble sulphur is thereby diminished. For instance, in a very careful experiment made on pure, finely-powdered sulphur in quantities of about ten grams, it appeared that the percentage content of insoluble sulphur was 4.01 before annealing, and 3.89 after annealing for several hours. A critical examination showed that this was entirely outside the limits of any possible experimental error. The annealing at  $90^{\circ}$  C. had been previously observed. We provisionally attribute the decrease of resistance to this partial annealing, which therefore tends to show that the conductivity of mixed sulphur has a maximum value somewhere between the 0 per cent. and 5 per cent. content of insoluble sulphur. The explanation of the temperature curve is, however, not by any means obvious, although it seems safe to draw the following conclusion, assuming that the temperature lag is inappreciable. The conclusion is that there must be at least two causes in operation influencing the resistance. One of these is probably the temperature *per se*, and the other the rate of transformation of insoluble into soluble sulphur, which is probably a complex phenomenon. The complexity may possibly arise from the change itself not being direct, the amorphous sulphur being first converted into a less stable form. There is also evidence, which will be given later, that at least two varieties of insoluble sulphur coexist in a rapidly cooled film.

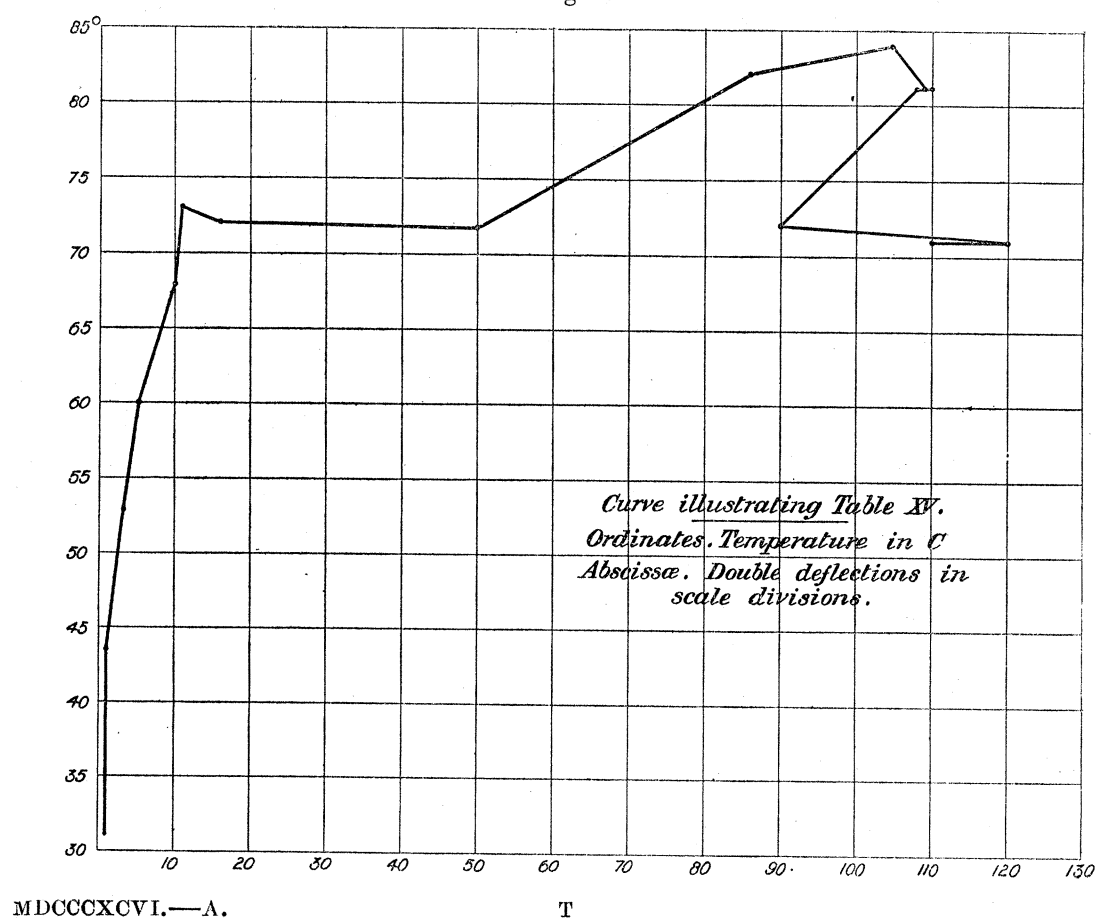
On referring to the table it will be evident that all the phenomena are similar to those formerly observed, but on a smaller scale, owing to the conduction being less. All the effects of time, of reversal of voltage, &c., were observed as before. We

append a short table giving the relation between temperature and resistance, by way of supplement to the general table of results.

TABLE XV.—Voltage, 280 volts.

Time.	Temperature.	Double deflection in scale division.	Remarks.
Not taken	31°	1 division = $4.9 \times 10^{-12}$ ampère	
"	44	1 "	
"	53	3 " (after 5 minutes)	All effects marked
"	60	5 " "	" "
"	68.2	10 " "	" "
"	73.4	11 " "	" "
"	72	16 " "	Difference due to temperature?
"	72	50 " "	After keeping at 72° for 10 minutes
3 hrs. 17 mins.	82	86 " "	
4 " 6 "	84	105 " "	
4 " 35 "	81.8	109 " "	
5 " 4 "	81.2	110 " "	
5 " 13 "	81.8	108 " "	
	72	90 " "	Cooling slowly
	71	120 " "	
7 hrs.	71.8	100 " "	Re-heated slowly (not slow enough?)

Fig. 4.



*Specific Inductive Capacity.*—Five pieces of film, measured as usual, gave the following values for the thickness in inches :—

(1) ·009022

(2) ·009917

(3) ·008689

(4) ·008058

Centre (5) ·008978

Mean ·0089316 inch = ·0226863 centim.

These measurements were made with very great care and represent the greatest accuracy the method is capable of; individual measurements of the same bit of film not differing by more than ·00008 inch. The differences are to be partly attributed to partial crushing or crumbling of the film during measurement, though there is clearly also a want of uniformity in the thickness of the film itself.

In obtaining the capacity by the DE SAUTY method, a balance was first obtained when the film was in the box, the lid was then taken off and a new balance obtained; and finally the plates were taken out and supported on their ebonite legs on the laboratory table at some distance from anything else. Removing the lid of the box changed the resistance required for balance from 2517·5 to 2510·5, and placing on the table reduced this to 2510. The connections and keys by themselves require 47 ohms in the adjustable arm. The other was always 100,000 ohms. We see from the small effect produced by lifting the plates out of the box which was to earth, that the free capacity may be neglected compared to the part of the capacity which is due to the dielectric action of the sulphur. We have used the factor  $2463/10^5$  in calculating the capacity, allowing for the capacity of the keys, &c. The standard required no correction at all, it was ·1 microfarad. The resulting capacity is therefore  $2463 \times 10^{-6}$  microfarad as stated in the summary. The sulphur condenser did not leak sufficiently to affect the galvanometer by more than one division with 300 volts, and hence with 40 Clarks may be considered to insulate perfectly. The mica standard, however, leaked quite appreciably, so that its resistance was only about  $2\cdot3 \times 10^{11}$  ohms. The capacity was measured again at  $71^\circ$ , and the balance was found to be unchanged. In this case the sulphur condenser also leaked, *i.e.*, its resistance was about  $10^{12}$  ohms, as against  $7 \times 10^{13}$ , say when it was cold. In order to find whether these leaks (which are of course exceedingly small) produced any measurable result, we made use of the formula given by GLAZEBROOK, 'Phil. Mag.' [5], vol. 1, p. 376-377, 1881. This is

$$\rho = \frac{R'\rho'}{R} \left( 1 - 2 \left\{ \frac{R'}{\rho'} - \frac{R}{\rho} \right\} \right)$$

where  $R$  and  $R'$  are resistances out in the arms, and  $\rho$  and  $\rho'$  the corresponding insulation resistances of the condensers. We found that the correcting factor was about

$1 + 8 \times 10^{-8}$  in one case,  
and  $1 + 2 \times 10^{-7}$  in the other.

Consequently our results are quite independent of leakage. Absorption, unless it be instantaneous, is guarded against by observing the point at which the kick vanishes.

Some doubt having arisen as to the correctness of the formula obtained by GLAZEBROOK, Mr. A. POLLOCK was kind enough to look into the matter for us. His conclusion is that instead of the formula quoted we ought to have

$$\rho = \frac{\rho_1 R_1}{R} \left\{ 1 - \left( 2 + \frac{R}{G} + \frac{R'}{G} \right) \left( \frac{R'}{\rho'} - \frac{R}{\rho} \right) \right\},$$

$G$  being the galvanometer resistance, the other letters retaining their meanings. This does not lead to any appreciable correction of our values.

Now, when the sulphur condenser is heated, the difference in the coefficients of expansion of sulphur and aluminium must lead either to the film separating from the aluminium or to both it and the aluminium being thrown into a state of strain. We know that the plates remained firmly attached to the film, from a subsequent examination, and, consequently, we are driven to admit that heating strains both the film and the plates. Now the coefficients of linear expansion as obtained from Sir W. THOMSON'S 'Collected Papers' (vol. 3, p. 209), which numbers were taken from "CLARK'S Constants of Nature," are for sulphur, say, '000063, and for aluminium, '000022. To be quite satisfactory, of course, the linear expansion of this particular kind of sulphur ought to be observed, but the values given (mean of those of FIZEAU and KOPP) are probably not very far wrong.

It is probable that when the aluminium plates are heated they are quite free to expand laterally and also vertically; in fact, the gold dish is so weak and soft, it may be set on one side, and the sulphur round the aluminium plates will, if anything, tend to drag them outwards. We may assume, therefore, that when the condenser is heated the aluminium plates increase in area, and are subject to some little stress, while the sulphur film increases freely in thickness, but is prevented, by sticking to the plates, from expanding beyond their limits. The film being thin and weak, compared to the plates, nearly the whole of the resulting strain is borne by it.

Consequently, any change in condenser capacity observed on heating will be due either to the direct effect of temperature change in altering dimensions or dielectric constant, or to the stresses thereby set up. We will assume the former alternative and see to what results it leads.

The facts are, that when the sulphur is heated, say from  $20^\circ$  C. to  $70^\circ$  C., the mica standard and resistance boxes being at constant temperature, no change in the balance is observed; for instance, it remains steady at  $2463 \times 10^{-6}$  microfarad within one figure in the last place.

The temperature coefficient of specific inductive capacity, which would be required to compensate for the alteration of capacity, computed from the variation of the various dimensions with temperature, is

$$\gamma = + 1.89 \times 10^{-6}.$$

This, of course, must be further investigated before we can regard it as a physical constant, but we may take it as pretty certain that there is either a temperature coefficient, or a strain coefficient, or both, or that the specific inductive capacity depends on the composition of the film, for the sulphur is partially annealed at 80° C., and, therefore, possibly at 70° C. It was a distinct oversight not to have tested this at the time by observing the capacity again when the sulphur was cold, and ultimately led to another experiment being undertaken for the special purpose of setting this question at rest. The result of this experiment was to prove that the specific inductive capacity of films, containing rather less insoluble sulphur than this, is distinctly greater the more insoluble sulphur they contain. Hence the temperature coefficient must be greater than the above if it is at all affected by the annealing, for the annealing would almost certainly have reduced the capacity.

While we used the old standard condenser the absorption was so great as to make the observations for capacity insufficiently exact for the present purpose.

## SECTION VI.

### *The Determination of Specific Inductive Capacity of Varieties of Sulphur by the Method of Weighing.*

In the prosecution of these studies by one of us and Mr. J. B. ALLEN, some experiments were made on the specific inductive capacity of sulphur by the method of weighing. In these experiments a good many sources of electrification suitable for the purpose were investigated, and a good many causes of error detected and rectified. The results, however, only referred to one plate, *i.e.*, to one containing 6.7 per cent. of insoluble sulphur, and even these results were not in such good agreement as could be wished. The best way of preparing plates of sulphur had, however, been discovered, and we felt sure that by gradually improving the apparatus, we should ultimately succeed in obtaining reliable results. The great merit of the weighing method, however, from our point of view, is that it makes the resulting value of the specific inductive capacity absolutely independent of any electrical measurements whatever. In the experiments previously described, we relied on the constancy of the voltage of Clark cells, on standardized resistance coils, and on certificated condensers. It was now felt that an absolute determination of one of the constants ought to be made by a perfectly independent method, in order to supply as complete a check as possible on the previous work. No method could have met our ends more perfectly than the method of weighing, for the result



remains entirely independent of the absolute value of anything (as a measurement of  $K$ , of course, should do); all that is required is a fairly accurate knowledge of the ratios of the weights employed, and of two distances which can be measured with fair accuracy. The drawback to the method is that it is not as susceptible of being carried to a high degree of accuracy as some more directly electrical methods.

Both measurements of length were reduced to the same standard, by fine callipers of ELLIOTT BROS., whose absolute indications are immaterial, but which we believe from other comparisons to be practically correct.

The comparison of the gilded brass and platinum weights with each other was carefully carried out on a fine balance, and resulted in showing that the weights were so well adjusted that none of the corrections observed can affect our results—the differences being much less than the error of weighing against the electric forces.

As we spent several months in perfecting our apparatus, after the experiments of Mr. ALLEN and one of us were finished, we decided to illustrate our description with a small drawing to scale (Plate 5), which we hope may be of assistance to other people using the method, and which will enable us to shorten our description considerably.

A is the zinc suspended disc. The lower surface was scraped true to a surface plate after the three pillars V, V, V had been soldered to its upper surface. The diameter of this plate was 12·65 centims., and it weighed (uncorrected) 154·3002 grams.

Each of the pillars V, V, V were bored and tapped so as to carry three screws—lying in a plane parallel to the plate. These screws are necessary to allow of the adjustment of the three fine German-silver wires, by which the plate is supported. It is necessary to have these screws well made if accurate and convenient adjustment is sought after. The point of junction of the three wires is attached to a single fine German-silver wire, which passes to below the balance case, where it is hung from a frame originally made for the purpose of weighing quartz rods in water, in order to determine their coefficient of expansion. This frame could be arrested just like the pan of an ordinary balance. The rough adjustment of the length of the wire was made by a minute box-wood shackle. The balance stood on a state shelf, and the rest of the apparatus on a slate table below it, and we may here remark that one of the first desiderata is steadiness and solidity in all the parts of the apparatus. A fine spiral of wire connects the plate to the guard-ring.

B is a guard-ring of zinc, the top and bottom surfaces being turned parallel to each other in a lathe. The inner diameter is 13 centims. and the outer diameter 23·6 centims., leaving the ring with a radial breadth of 5·3 centims. The clearance on each side of the suspended plate is, therefore, ·175 centim. We could have done with less clearance than this, but an examination of the theory showed that no error at all comparable with those of measuring and weighing would be introduced by an annular space of these dimensions.

The guard ring is supported by three strong legs, C, C, made of zinc, and provided with good levelling screws and jamb nuts, D, D. The ring is put to earth by a soldered connection, which ultimately is soldered to a water-pipe. The high potential plate E is a large glass disc, 30.5 centims. in diameter, and optically flat. It was originally silvered, but the silvering having gradually tarnished by contact with sulphur, and its conductivity having become unreliable, it was replaced by some good thin tin-foil, fastened down with thin starch paste, and put on so well that no appreciable deviation from flatness could be detected. It was attached by a clamp and wire, H, to the high potential end of the transformer. The thickness of the plate, 3.3 centims., gets rid of any fear as to flexure producing an appreciable effect.

This plate was supported by three ebonite cones, J, J, 2 centims. in diameter at the thick part, and 5.4 centims. long. These cones were got to insulate well, they were supported by a wooden stand, K, triangular in shape, and carried in turn on three levelling screws, working through brass fittings, and bearing on brass caps supported by three of the double glass and paraffin insulators, M, M, M, we have had occasion to refer to so often before. All this part of the apparatus requires to be well and substantially made, or it tends to tilt over a little. The top of the glass disc was 22.5 centims. above the slate bench. The wire connecting the tin-foil to the transformer was short and thick, but it was found that no alteration was made by twisting it into a spiral, so that no "resonance" effects are to be feared.

Screens of tin-foil pasted on to cardboard completely surrounded all parts of the apparatus. The first screen stood on the guard ring and enclosed the back of the suspended plate, allowing the wire to pass through a small hole. Outside the whole affair was another and larger screen. Both these screens were cylindrical and properly shaped, and were made in two parts joined by tin-foil flaps. The balance was also completely encased in a screen of tin-foil and gauze, allowing the pointer to be observed with ease. The panels of the balance case were separately screened by gauze to allow of the adjusting of weights, &c. The elementary mistake of having bad screen connections was not made. Screens are very necessary to prevent air currents, as well as to hinder electrostatic action. The balance was in a room with a south aspect at the opposite end of our building to the room occupied by machinery.

*Balance.*—This was a rather short arm balance, which was formerly used for weighing quartz, &c. It has a high range of sensitiveness, though this was diminished to a convenient amount in order to secure other advantages. It was furnished with an adjustable screw stop at R, by Mr. ALLEN. The balance will carry 1 kilogram, so that there is no danger of warping.

*Electro-Dynamic Action.*—This was tested by insulating the glass plate, the other plate being connected to earth on one side, and to the terminal of the transformer on the other. No trace of any action could be detected, *i.e.*, either nothing at all or else something incomparably smaller than we could approach in the experiments on weighing.

*Auxiliary Condenser.*—This is necessary to swamp the effect of the changes in capacity produced by putting in or taking out the sulphur. We used ten “gallon” Leyden jars in parallel with the guard-ring condenser.

*Transformer.*—It appeared from the experiments of one of us and Mr. ALLEN, that of all the methods of excitation tried, nothing was so steady as a large coil used as a transformer, the alternator being excited by a small current only, and driven by rather loose belting from a well loaded gas engine which has a short period of irregularity. The alternator has a very massive field-magnet system which rotates, and this acts sufficiently well as a fly-wheel to smooth most of the irregularities of the gas engine, when these are short in period. Some irregularities, however, remain and impose the limit to the accuracy attainable. It was found best to have a weak field on the alternator, and use all the armature coils, instead of strongly exciting it and using a few armature coils in series with resistances.

This was contrary to expectation. The induction coil could also be used with its break, or with a clock-work break. Mr. ALLEN found, however, that these were not so steady, and the same remark applies to a number of attempts made to use a WIMSHURST machine driven at a constant speed, and having one terminal permanently to earth, and the other earthed by a high resistance vacuum tube, with a bit of caustic potash in it. An irregular excitation will very quickly spoil the knife edges of the balance. The frequency of the alternator was about 60, and we got better results with this than when the frequency was less.

In order to keep a check on the voltage, the latter was measured continuously by a KELVIN static voltmeter reading to 12,000 volts. About 5000 to 6000 was the voltage generally employed,

*Adjustments.*—The apparatus having been provisionally set up, and all rough adjustments made, the following procedure was adopted. The glass plate was levelled as accurately as possible by an ordinary laboratory spirit-level, reading perhaps to something like 30'' of arc. The guard-ring was then similarly levelled at a suitable distance, from 1.5 to 2 centims. in our experiments, from the lower plate. This was then checked by measuring the distance between the top of the tin-foil and the bottom of the guard-ring, in several places by a wedge reading to .1 millim. directly. The adjustment being found correct, the hanging plate was adjusted to the guard-ring by eye, the under surface of the ring being flat and level, and the suspended plate also being flat. This can be done with great accuracy, just as in sighting a barometer. Of course the preliminary adjustment was good enough to let the plate hang concentrically in the guard-ring. The adjustment must be made with the plate counterpoised, and is rather tedious, but presents no difficulties that may not be overcome by patience. The lower plate was then excited in order to find if the suspension stretched appreciably, but this was found not to be the case. The screens were then placed in position, and the experiment was ready for observation.

*Sulphur Plates.*—These were made in two ways, and we consider that too much care cannot be exercised in this part of the work.

*“ Insoluble ” Plates.*—A light sheet zinc mould was prepared, capable of containing a plate about two inches greater in diameter than the one to be employed (which was made usually of rather larger diameter than the guard-ring), and say four or five times as thick. The sulphur, previously filtered as described, through glass wool and platinum gauze, was melted and raised to a sufficient temperature by placing the zinc mould on a hot flat plate. It was noticed that after the filtered sulphur was cold, when it was being broken up for the final melting, it still possessed a strong sulphury smell, which in this case suggested gas lime. This shows that there is an advantage in distilling the sulphur, although the amount of impurity present may be imperceptible on boiling away the filtered sulphur in a polished platinum dish. However, the impurity seems to be got rid of by re-melting in the dish, for the smell was not detected on breaking up the plates at the close of the experiments.

The mould having been filled with sulphur at the proper temperature, *i.e.*, after it had become very viscous, above  $170^{\circ}$  C., the whole affair was plunged into cold water and agitated so as to cool it as quickly as possible. When the plate was sufficiently stiff, *i.e.*, after some hours, the mould and sulphur were mounted on a lathe, and the bottom of the mould cut completely away, till only a flat surface of sulphur was left. This was then reversed on the face plate, and the free surface turned down till we reached a homogeneous part of the sulphur, or beyond that if desirable. A round cake of the desired size was then cut out. The first plates were then scraped to a surface plate; but it soon appeared that the natural warping of the plates rendered this an unfruitful labour. Consequently our later practice was to grind the plates down on a sheet of glass-paper, glued to a flat (really flat) iron plate, till they were true to a straight edge. It was necessary to experiment at once before the plates warped too much.

*Soluble Plates.*—These cannot be handled so freely as plates consisting partly of soluble and partly of insoluble sulphur, however we found the following method gave just as perfect results. The mould consisted of a flat plate of “opal” glass, which is very smooth and generally better than ordinary sheet glass. A ring of plaster of Paris was cast on such a plate and dried, then previously annealed sulphur was carefully heated to just above the melting-point and poured into the mould levelled by the glass plate. The sulphur was caused to cool as fast as convenient, in order to prevent the formation of internal cavities. The plate, when cold, left the glass and plaster easily, and it was, of course, much larger than requisite. In order to prepare the upper surface, the plate was held down flat on the bed of a BROWN and SHARPE milling machine, and milled at a good speed till it was homogeneous and of the proper thickness. This gives just as good a flat surface, or rather better, than any of our lathes, and leaves a very fine appearance. Owing to the rapidity of cooling, any

impurity from the plaster of Paris is localized to the edge of the plate, *i.e.*, is about half an inch outside the guard-ring, where it can do no harm during the weighing.

*Warped Plates.*—One of our plates warped in a very regular manner, so as to become concave on one side and convex on the other ; the curvature looked spherical and was assumed to be so.

As we did not know what error this might lead to, and still did not wish to lose the plate—on which a good deal of time had been spent—we measured the curvature by a spherometer, and Mr. POLLOCK kindly investigated for us the proper formula. As, however, it involved a difficult integration, it was considered advisable to calculate the effect on the value of  $K$  of some extreme assumption as to the thickness of the plate. For this purpose it was supposed that the plate increased in thickness by the same amount all over, as at the boundary of the suspended plate. The radius of curvature was found to be for the concave side of the plate, 133·234 centims. ; and for the convex side, 134·177 centims. ; and the thickness of the plate was ·94 centim. The diameter of the plate was taken at 5 inches = 12·70 centims. In a particular experiment it was found that the value of  $K$ , when the plate was considered as having the maximum effective thickness of ·94407 centim. instead of ·943 centim., would be 3·6836, instead of 3·6878 when the measured thickness was taken. Since this difference is outside the experimental limits of weighing or measuring, and is itself probably so far in excess of the actual correction, even if the lines of force are appreciably “refracted,” we decided to ignore the effect of the curvature.

*Method of Experimenting.*—The experiment consists in observing the attraction in grams weight on the suspended disc, both when the sulphur plate is in and out. To begin with, everything must be carefully dusted, to get rid of shreds of all kinds, and the hanging plate counterpoised—it weighs, as has been stated, about 154·3 grams. The current is then turned on and observed to be steady by the voltmeter—it never really gets steady, the voltmeter oscillating through about one division, corresponding to, say, a “permanent” variation of half a division or 100 volts in 5000, or say, 2 per cent. ; this would cause the force to vary by 4 per cent.—this is an extreme limit to the fluctuations. Weights are added until the pointer of the balance is observed just to incline to leave the zero—of course, as soon as it does leave it the force diminishes and the balance tilts over. The point having been ascertained as nearly as possible, the rider is run down to increase the weight by ·005 gram, and if this produces a decided tilt, the observation is taken as exact. This means that the force can not be measured to less than the weight of 5 milligrams owing to fluctuations of potential difference. The forces to be observed vary from about ·5 gram weight without the sulphur to 2 grams with it, and these forces appear in the final result as a ratio which enters to the power of one half. The uncertainties of weighing, therefore, amount to about ·005 gram in one gram, or, say, ·5 per cent., and affect the value of  $K$  to about ·25 per cent.

The attraction, without the sulphur, having been observed, the attraction is again measured with the coil commutator reversed, in case there is any outstanding electrification; in general this produces no effect. There was no difference in any of the experiments leading to our values.

The next step is to earth the high potential plate and carefully dust every part of the apparatus, including the sulphur plate; the connecting wire is dusted by running a flame along it. The sulphur plate is then inserted, and an observation made of the value of the counterpoise, in order to find if there is any free electrification. If there is, the plate is taken out and the electrification removed by a flame—a risky proceeding, and one we never indulged in unless it was absolutely necessary. The process of finding the balance was then repeated as before. When a sufficient number of observations, both with the plate in and out, had been made, the screens were removed, and the distance between the guard-ring and the glass plate remeasured. There was never a difference of more than .1 millim. At the end of the series of experiments all the plates available were experimented on in this manner one after the other, so as to get good comparative results. The apparatus was then dismantled, and the distance between the fixed and suspended plate changed, after which the adjustments were re-made and the whole series gone through again at the new distance, with a view to eliminating accidental errors of setting, weighing, and measuring.

The sulphur plate must not be less than five or six millims. from the suspended plate, or the free electrification at its upper surface has a sufficient P.D. from that of the earth to cause brush discharges. Consequently we always examined some plate or other in the dark to see if this did occur. If it does, of course, the result is that we get too low readings and a too low value of  $K$ . On the other hand, the nearer the top of the sulphur plate is to the suspended plate the better, for the greater the forces to be observed. The “art” of the experiment, we should say, lies in adjusting the voltage till brushing just does not occur. This is also provided for by placing the coil terminals so near together that a discharge occurs there before it occurs between the sulphur and the earthed part of the apparatus. It is also exceedingly necessary to remove all dust and sulphur crumbs between each set of weighings.

On thinking the matter over in the light of our present experience, we have an idea that there might be advantages in using a liquid of high electric strength instead of air—in fact, to proceed as QUINCKE did in determining the dielectric constants of liquids by weighing, in order to get the advantage of the large forces he was able to measure.

Analyses of the sulphur plates were made by breaking them up, and taking samples from the active part. This was also necessary in order to find out whether there were any cavities in the plates. In only one plate was a cavity discovered, but happily it was under the guard-ring almost entirely, and was very insignificant.

The partly insoluble plates were annealed in some cases in order that the difference of specific inductive capacity might be observed in one and the same plate. The annealing produced both buckling and cracking; the latter does not matter, and the former has been dealt with. In cases where the plates were annealed the analysis was made on samples collected during the turning or milling of the final surfaces. The formula of calculation is best given in the following form :—

$$\frac{F}{F_1} = \left( \frac{\rho_1 + \rho_2}{\rho_1/K + \rho_2} \right)^2,$$

where  $F$  and  $F_1$  are the forces observed,  $(\rho_1 + \rho_2)$  is the distance between the fixed and suspended plates,  $\rho_1$  is the thickness of the sulphur, and  $K$  is the quantity we are in search of. The results will be sufficiently evident from the following table, which includes unsatisfactory values as well as satisfactory ones. The former are included with a view of showing how we gradually improved our results as we eliminated various sources of error—bad conductivity of silver coating, irregularity of driving, effect of brushes due to imperfect dusting, or too high voltage, &c., &c.

TABLE XVI.—Summary giving Details of Measurements for K by Method of Weighing.

Date.	Temperature. ° C.	Thickness of cake, $\rho_1$ .	Distance between plates, $\rho_1 + \rho_2$ .	Mean ratio of tensions.	Maximum error in ratio as per cent. of mean ratio.	Values of K.	Mean K.	Per cent. of in- soluble sulphur.	No of set.	Remarks.
1893. May 26 . . . " 26 . . .	17.0 17.0	centims. 0.943 0.943	centims. 1.45 1.73	3.597 2.751	per cent. 5.01 3.0	3.66 } 3.68 }	* 3.67 Rejected	per cent. 1.069	(1)	This cake was made from C—S distilled twice. It was made in a zinc dish, May 23, the S being poured in when thick and black, and the whole cooled by immersion in water. The water was not allowed to cover top of cake. It was turned up in the lathe. Diameter about 20 centims. Analysis made of last cut from top and bottom mixed. On breaking up cake (July 6) it was found to be solid all over. Analysed June 30.
" 30 . . . " 30 . . .	19.1 19.1	0.945 0.945	1.73 1.42	2.551 3.5716	6.31 5.74	3.169 } 3.419 }	* Rejected	0.0	(2)	Rejected from doubts regarding silvered glass plate The above cake (1) annealed for 5 hours at 105° C. in thermostat. Cake became buckled and cracked along about three-quarters of a diameter, otherwise quite sound. Analysed and broken up on July 6. Results rejected owing to large per cent. of error, due to defects in silvered glass plate, &c.
June 2 . . . " 2 . . .	15.0 15.0	1.2476 1.2476	1.50 1.30	6.7192 3.7014	1.81 4.65	3.820 } 3.727 }	* Rejected	1.437	(3)	Cake of C—S filtered through platinum gauze and glass wool. Kept just molten for 2 to 3 hours and then cast on an opal plate inside a plaster of Paris ring. Not immersed in water. The bottom surface being flat the top one only was ground flat on glass paper. The sample for analysis was taken on June 28. Cake made on June 2. It was broken up, after annealing, on July 6, and only one cavern found in the cake near one edge, and certainly in that part which was under the guard ring (3), (4), and (5) are sets made with this cake. All have been rejected owing to large error, owing amongst other things, to glass plate not being properly silvered
" 5 . . . " 5 . . . " 5 . . .	15.1 15.1 15.1	1.2476 1.2476 1.2476	1.90 1.68 1.50	3.401 4.5787 5.958	4.30 0.53 3.12	3.2756 } 3.536 } 3.44 }	* Rejected	1.437	(4)	The value K = 3.536 in set (4) is the only reliable one, as per cent. error in ratio is > 1 per cent. of mean ratio has been rejected
" 13 . . . " 13 . . .	17.3 17.3	1.2476 1.2476	1.88 1.68	3.731 4.6736	2.92 1.65	3.65 } 3.58 }	* Rejected	1.437	(5)	error in ratio is .53 per cent. only. Any value in which per cent. error in ratio is > 1 per cent. of mean ratio has been rejected
" 23 . . . " 23 . . .	13.5 13.5	1.195 1.195	1.68 1.88	4.470 3.5094	1.32 1.31	3.86 } 3.75 }	* Rejected	3.049	(6)	Cake of C.S. filtered through platinum and glass wool. Made as (1), not immersed overhead in water. Turned up in lathe. Made June 20. Seems very solid. Has not been broken up. Analysis made of last cuts front and back. This set rejected owing to large per cent. error in ratio. Analysed June 30.
" 25 & 26 " 25 & 26	13.5 14.0	1.195 1.195	1.88 1.71	3.5035 4.216	0.01 0.31	3.74 } 3.76 }	3.75	3.049	(7)	This set was in a measure preliminary Same cake as last (6). The following sets are to be taken as final, and having been made with all the precautions suggested by experience. The glass plate used for H.P. plate has been covered with tinfoil instead of silver
" 25 & 26 " 25 & 26 " 25 & 26 " 25 & 26	13.5 14.0 13.5 14.0	1.2476 1.2476 0.945 0.945	1.88 1.71 1.88 1.71	3.5935 4.436 2.32 2.6	0.54 0.45 0.00 0.00	3.46 } 3.56 } 3.16 } 3.20 }	3.51 3.18	1.437 0.0	(8) (9)	Same cake as (3) Same cake as (2), i.e. C—S twice distilled (originally insoluble) and annealed at 105° C. for 5 hours. See remarks on (2). Analysed July 6
July 5 . . . " 5 . . .	13.0 13.0	1.223 1.223	1.70 1.91	3.9303 3.1	0.33 0.00	3.214 } 3.074 }	3.144 Mean, 3.162	0.0	(10)	Cake (3), (8) made by casting C.S. (filtered). This cake (3) was annealed at 105° for 4½ hours in thermostat. It did not buckle in any way, but split all along a diameter and in a few other places. With care a set of readings was taken as shown. Analysed July 6. Annealed June 28

NOTE.—Rejected values marked \*.



The net result of the measurements detailed in Table XVI. is as follows :—

Temperature, $14^{\circ}$ C.	
For mixed sulphur containing 3 per cent. of insoluble sulphur .	$K = 3.75$
"      "      "      1.43      "      "      . .	$K = 3.51$
Completely soluble sulphur (aged monoclinic ?) . . . . .	$K = 3.162$

The value of  $K$  for the soluble sulphur is the mean of values obtained on two different samples.

It would appear from these values that the specific inductive capacity rises as the percentage of insoluble sulphur increases.

Experiments have yet to be made on a cake of sulphur containing a very large amount of insoluble.

The results of the experiments described in the foregoing investigation may be summarized as follows :—

(1.) The specific resistance of perfectly soluble sulphur, either simply monoclinic, or aged monoclinic, *i.e.*, monoclinic sulphur which has lost its crystallographic properties and become opaque, but which practically preserves its old melting-point, is very high, certainly above  $10^{28}$  C.G.S. units.

(2.) An admixture of say 5 per cent. of amorphous sulphur reduces this great specific resistance to say  $10^{25}$  C.G.S. units.

(3.) The conductivity, such as it is, is marked by some peculiarities; it tends to be discontinuous, resembling in this the behaviour of surface films and of bad conductors (glass rods and ebonite) generally.

(4.) The conductivity is always much greater for some time after the battery is reversed, say for three or four minutes.

(5.) The "residual" charge, when the sulphur is regarded as a dielectric, is small.

(6.) The conduction does not obey OHM's law. The specific conductivity is greater, the greater the voltage.

(7.) The specific inductive capacity of mixed sulphur is greater than of pure soluble sulphur.

(8.) The conductivity of mixed films increases enormously while they are annealing, and even perfectly crystalline sulphur shows traces of conductivity at temperatures near the melting-point.

(9.) Melted sulphur conducts comparatively well, say 1000 times as well as a cold mixed film.

NOTE ADDED APRIL 1, 1895.

*Experiments made March and April, 1894.*

A possible explanation of the very divergent values of K, as exhibited by different modifications of sulphur, may be sought in the corresponding variations of density.

To test this point, an examination was made of the density of the sulphur employed in the experiments for K by weighing. The accuracy of the determination of density extends to the third figure at least.

The following table will show that the variation of specific inductive capacity is not to be explained by supposing that it is merely proportional to density.

TABLE showing Relation between the Specific Inductive Capacity and the Density of the Forms of Sulphur.

Description of plate.	Specific inductive capacity of plate.	Density of plate.	Specific inductive capacity $\div$ density.
Pressed cake, containing 90 per cent. of insoluble amorphous sulphur . .	2.194	1.11	1.976
Cast cake, containing 3 per cent. of insoluble sulphur . . . . .	3.75	2.001	1.874
Cast cake, annealed, containing no insoluble sulphur . . . . .	3.18	2.0103	1.582

## DESCRIPTION OF PLATE 1.

### *New High Grade Galvanometer.*

Fig. 1. *Elevation.*

- A. Fine adjustment in azimuth for control magnets.
- B. Coarse adjustment for raising or lowering same.
- C. Fine               "               "               "
- D. Brass frame or bridge carrying control system.
- E. Iron slabs forming magnetic screen.
- F. Wooden stand carrying iron slabs.
- G. Brass ring carrying D, supported by three levelling screws on lead pillars, H.
- H. Lead pillars carrying G.
- I. Ebonite slab insulating and supporting coil system (*e, e, &c.*, fig. 2).
- J. Glass and paraffin insulators supporting ebonite slab I.
- K. Concrete slab supporting the whole apparatus.
- L. Sandstone pillar supporting K.
- M<sub>1</sub>, M<sub>2</sub>. Top control magnets.
- N<sub>1</sub>, N<sub>2</sub>. Bottom control magnets.
- O. Wooden carriage for N<sub>1</sub>, N<sub>2</sub>.

Fig. 2. *Section.*

A—O. Same as in fig. 1.

Q. Position of millboard case enclosing the coils, &c.

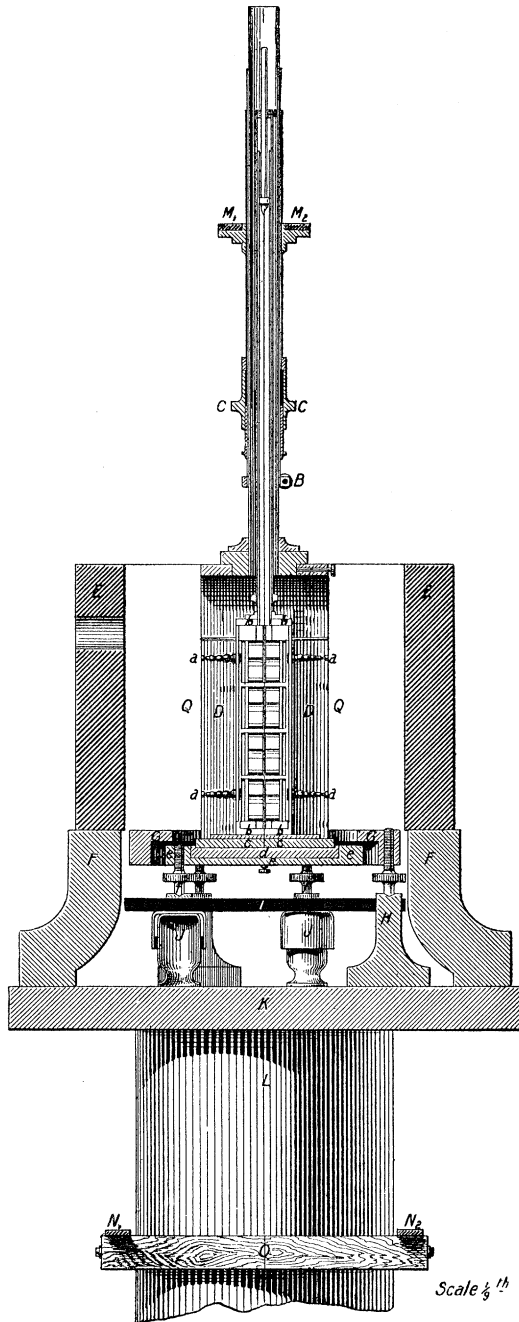
Details of coils and mounting (small letters).

- a, a.* Ebonite terminals.
- b, b.* Brass frames carrying coils.
- e and d.* Brass base.
- e.* Brass cell, in which the whole of the coils and magnet system are free to turn.
- f, f.* Levelling screws.

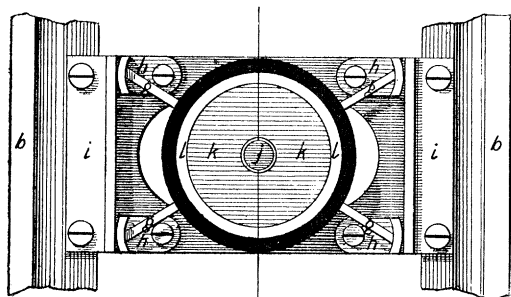
Fig. 3. *Coil support in plan and section.*

- a, a.* Ebonite terminals.
- b, b.* Brass frame.
- g, g.* Quartz rods supporting coil.
- h, h.* Brackets carrying quartz rods.
- i, i.* Carriage fastened to *b, b*, but adjustable to magnet system by leaving a play in the holes.
- j.* Magnet forming part of system.
- k.* Wire forming coil.
- l.* Paraffin mounting.
- n.* Ebonite mounting.
- m.* Glass front supporting a pair of ebonite pillars, *a, a*.

Fig. 1.



COIL SUPPORT  
Half Size.



PLAN

Fig. 2.

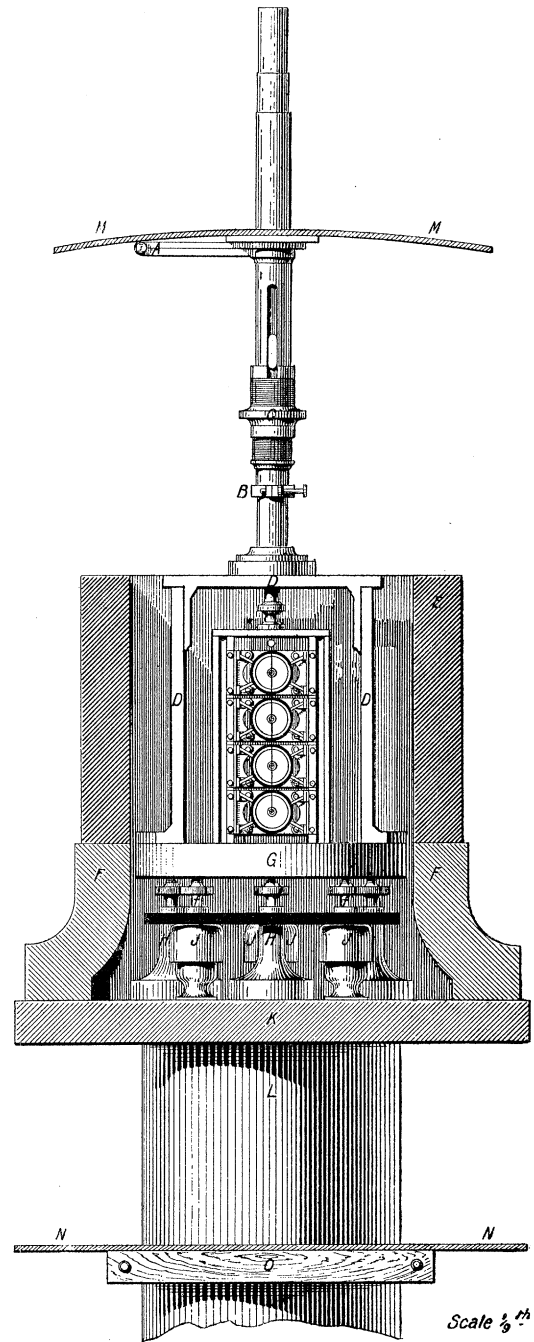
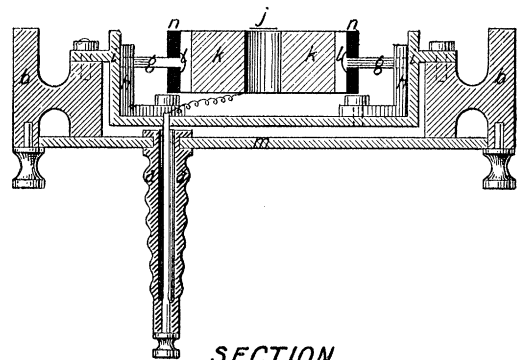


Fig. 3.



SECTION

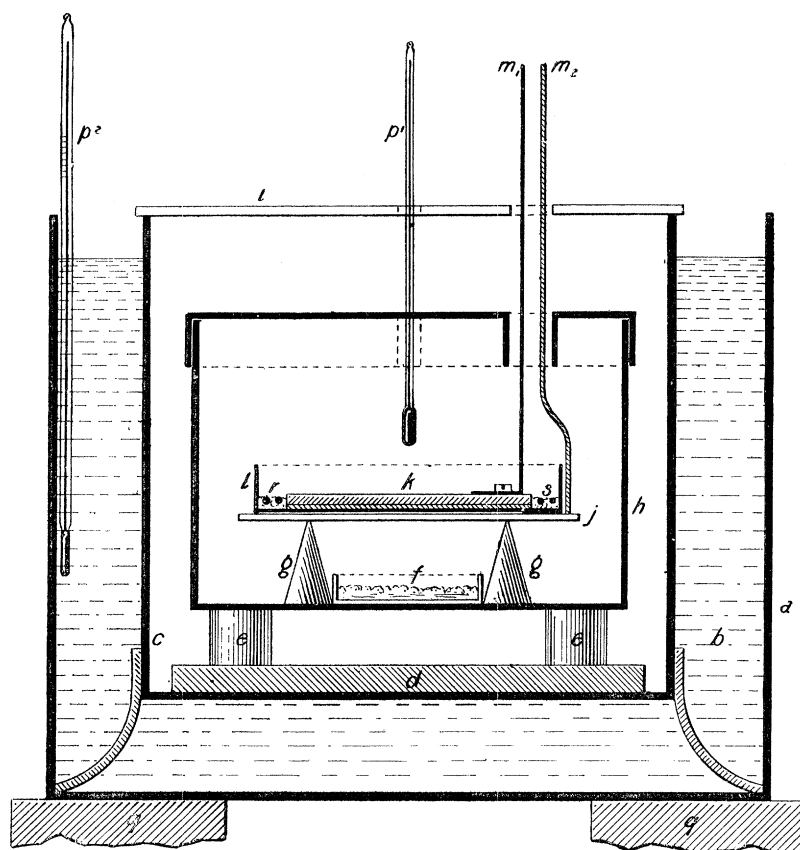
Shewing Insulation of Terminals.

## DESCRIPTION OF PLATE 2.

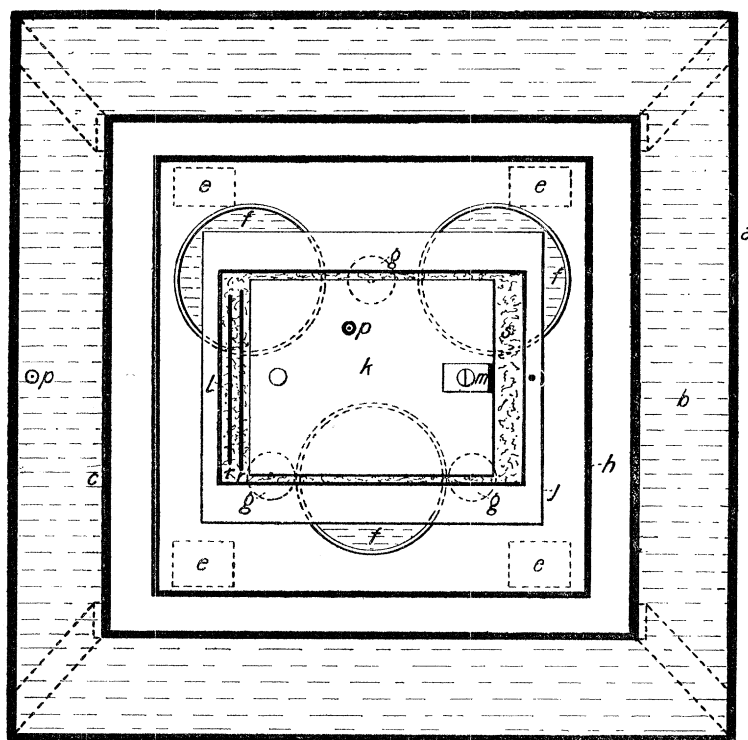
Fig. 1. Thermostat. A. Section. B. Plan.

- a.* Outer case of brass.
- c.* Inner case of brass silvered inside.
- b.* Heavy mineral oil filling annular space between *a* and *c*.
- d.* Lead weight to keep *c* in position.
- e, e.* Ebonite blocks to support *h*.
- f, f.* Dish with drying material.
- g, g.* Ebonite cones supporting and insulating glass plate *j*.
- h.* Innermost brass box, with lid, silvered inside and outside. Holes in lid for thermometers and electrodes. Space between *h* and *b* filled with air.
- i.* Glass cover.
- j.* Glass plate supporting gold dish and sulphur.
- k<sub>1</sub>, k<sub>2</sub>.* Aluminium plates forming armatures of condenser (see fig. 5, Plate 3).
- l.* Zinc dish supporting an inner gold dish (see fig. 5).
- m<sub>1</sub>, m<sub>2</sub>.* Electrodes from upper and lower aluminium plates.
- p<sub>1</sub>.* Standard thermometer.
- p<sub>2</sub>.* Ordinary high range thermometer.
- q, q.* Brick supports.
- r, r.* Quartz sticks in sulphur.
- s.* Surplus sulphur.

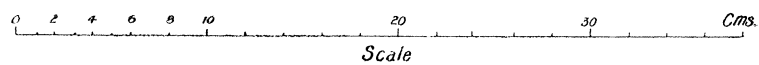
Fig. 1.



A. SECTION.



B. PLAN.



### DESCRIPTION OF PLATE 3.

Fig. 2. Four-pole ebonite key.

- $\alpha$ . Wooden base.
- $b, b, b, b$ . Ebonite rods with mercury cups in upper ends.

Fig. 3. Reversing key, &c.

- $\alpha$ . Wooden base.
- $b, b, b, b$ . Ebonite rods and mercury cup in upper ends.
- $c, c$ . Rods of fused quartz mounted in ebonite ends, and with mercury cups.
- $f$ . Tin-foil wrapped on ebonite handle.
- $d$ . Discharging point, only used when determining residual charge to connect  $g'$ ,  $g^2$ , thus instantaneously discharging condenser.

For resistance measurements the legs at opposite corners were metallically connected as usual in a commutator.

Fig. 4. Micrometer telescope used with new galvanometer.

- $\alpha$ . Object glass.
- $b$ . Graduated micrometer head.
- $c$ . Scale divided on glass, replacing usual comb.
- $d$ . Movable spider line.
- $e$ . Eye-piece.
- $f$ . Brass mounting, carries  $\alpha$  and  $e$ , and is capable of a universal motion (not shown).

Fig. 5. Gold dish and aluminium plates.

- $\alpha$ . Aluminium handle used to lift  $K_1$  when making film. This is removed and replaced by electrode  $m$  when film is in position.
- $K_1, K_2$ . Aluminium plates between which the sulphur film is formed.
- $l$ . Outer zinc dish.
- $c$ . Inner gold dish supported by  $l$ .
- $s$ . Surplus sulphur.
- $r, r$ . Quartz rods in sulphur.

NOTE.—Since the sketch was made, a zinc dish has been fixed to the upper aluminium plate  $K_1$ . It is scraped true on the bottom and joint sealed with sulphur. The dish can then be filled with pounded ice, when making mixed sulphur films.

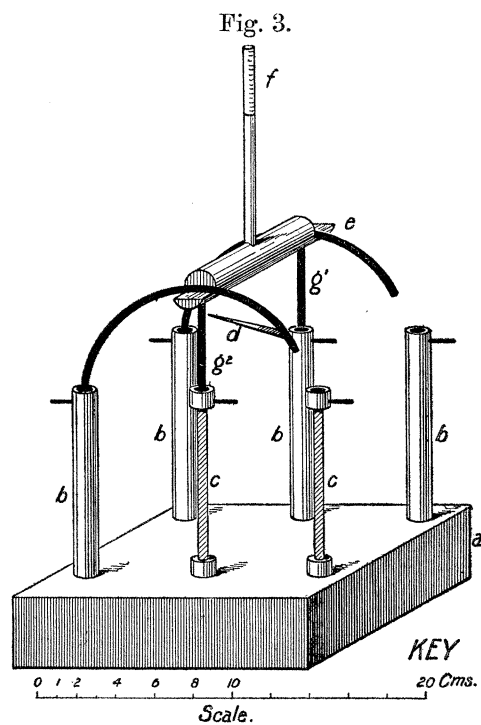
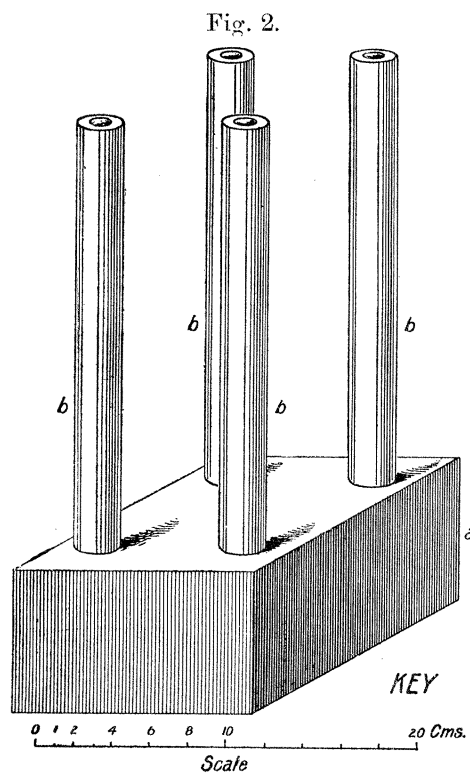
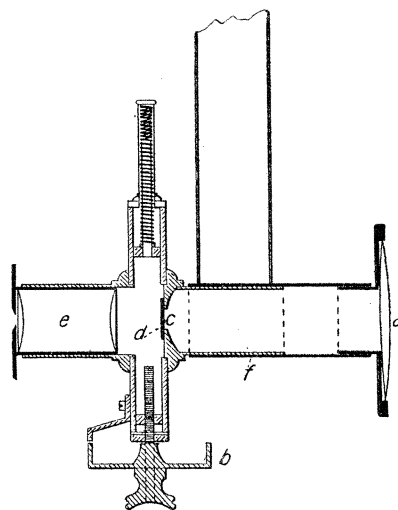
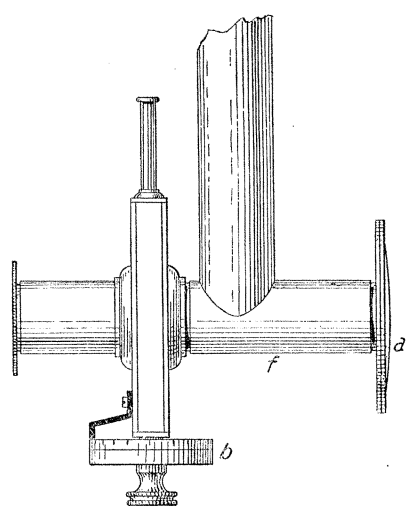


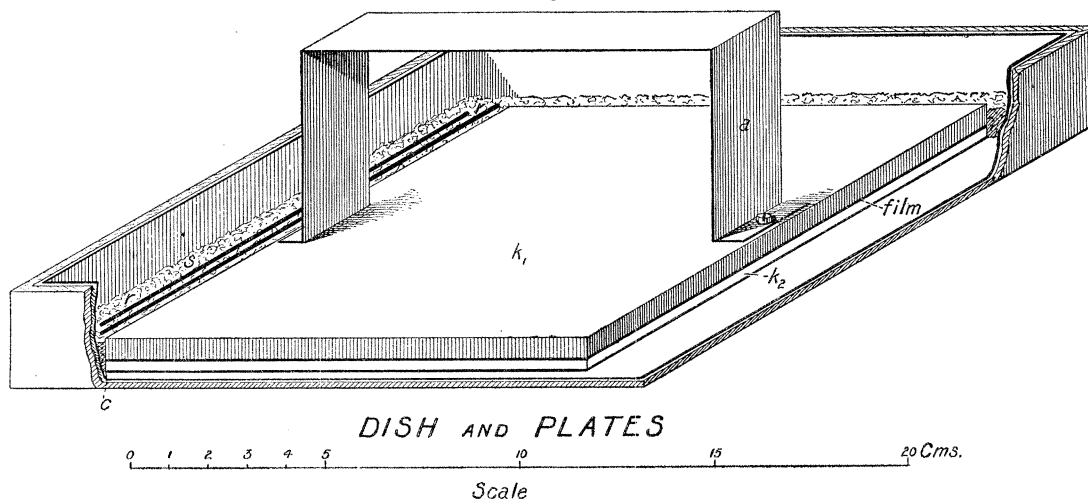
Fig. 4.



MICROMETER

Scale 0 1 2 3 4 5 10 15 20 Cms

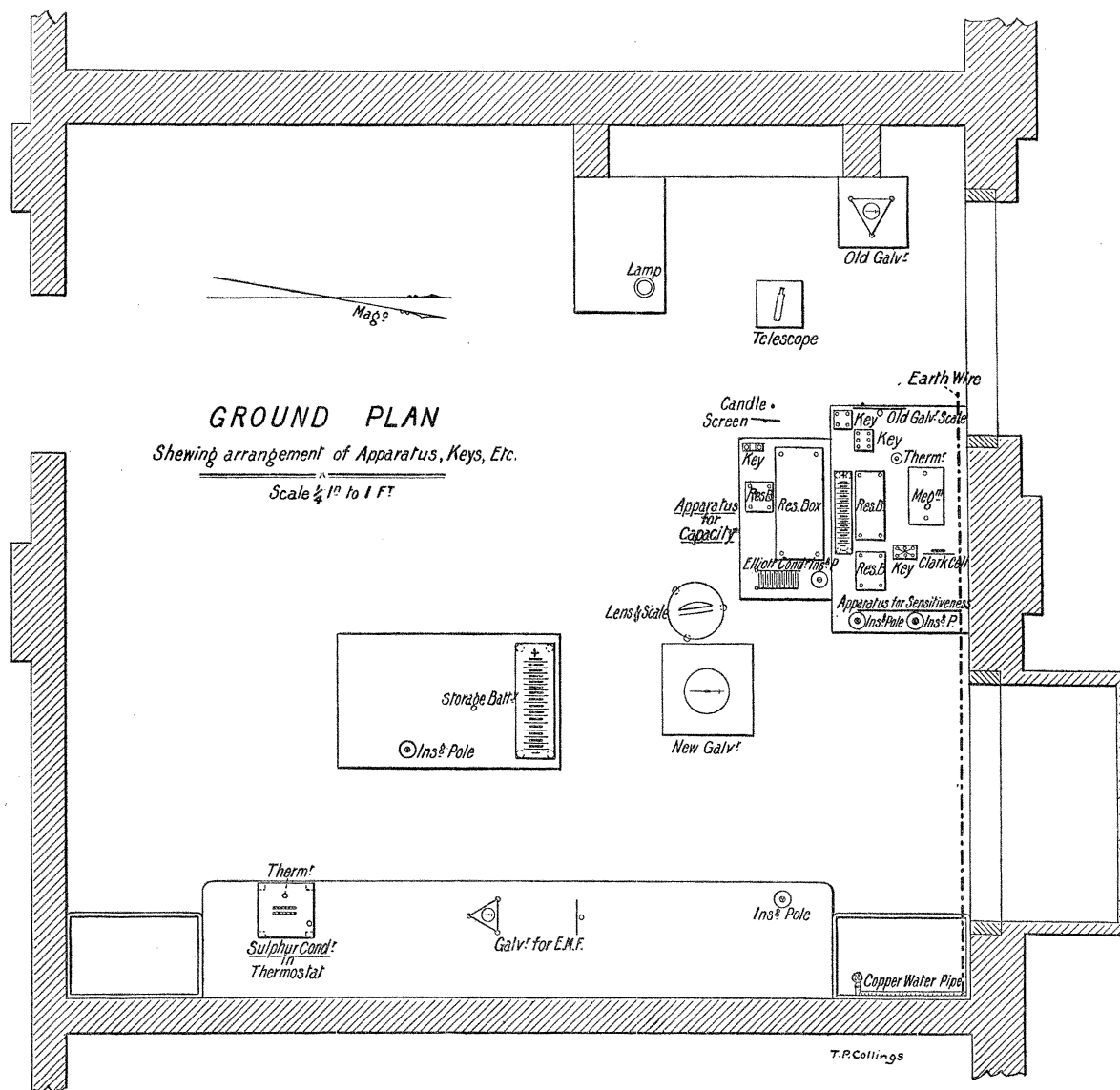
Fig. 5.



DISH AND PLATES

Scale 0 1 2 3 4 5 10 15 20 Cms.





## DESCRIPTION OF PLATE 5.

- A. Suspended zinc plate attached to balance arm. Connected to earth by a flexible spiral of No. 40 wire, B.W.G.
- B. Guard-ring of zinc with parallel faces.
- C, C. Zinc legs attached to B by brass screws.
- D, D. Brass levelling screws with lock-nuts, for levelling guard-ring.
- E. Glass plate covered with a sheet of tin-foil F, which forms the high potential armature of the condenser.
- F. Tin-foil surface attached to flat glass plate E.
- G. Cake of sulphur.
- H. Connection from F to the induction coil.
- I. Metallic connection from legs of guard-ring to outer tin-foil case and *earth*.
- J, J. Ebonite pillars supporting glass plate.
- K. Wooden base supporting J, J, and E.
- L, L. Levelling screws by which the tin-foil surface may be brought level and parallel to A.
- M, M. Glass and paraffin insulating stands supporting the three levelling screws, L, L, L.
- N. Millboard box coated inside and out with tin-foil, and protecting the back of the suspended disc from induction.
- P. Large millboard box coated with tin-foil, and surrounding all the apparatus. It is put to earth, as is N.
- Q. Metallic casing surrounding the balance.
- S. Condenser in parallel with secondary terminals to swamp the capacity of the sulphur condenser.
- T. High potential Kelvin voltmeter.
- X. High potential terminal of secondary.
- Y. Low potential terminal of secondary, put to earth on water main. The same earth connection is made throughout.

SPECIFIC INDUCTIVE CAPACITY OF SULPHUR  
By Weighing.

