On the Clark Cell as a Standard of Electromotive Force

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XV. *On the Clark Cell as a Standard of Electromotive Force.*

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[PLATE 16.]

Summary of Contents.

PART I.—THE ABSOLUTE ELECTROMOTIVE FORCE OF A CLARK CELL.

PART II.—COMPARISON OF VARIOUS FORMS OF CELLS AND OF THE MATERIALS USED.

Part I.—On the Absolute Electromotive Force of a Clark Cell.

§ 1. *Introduction.*

The experiments recorded in the following paper were undertaken with the object of testing various points in the manufacture and use of the Clark cell as a standard of electromotive force, specially with a view of investigating the most simple method of setting up a number of such cells which should have, within certain limits, a definite electromotive force, and of determining the limits within which, it is safe to say, that the E.M.F. of such a cell will lie.

We have also determined afresh the relation between the E.M.F. of a Clark cell and the electrochemical equivalent of silver. The experiments have been conducted in the main on the lines of those described in Lord Rayleigh's papers "On the Electrochemical Equivalent of Silver and on the Absolute Electromotive Force of Clark Cells" ('Phil. Trans.,' Part II., 1884), and "On the Clark Cell as a Standard of Electromotive Force" ('Phil. Trans.,' Part II., 1885).

The investigation was undertaken in connection with the work of the Committee appointed by the Board of Trade on Standards for the Measurement of Electricity.

Resolution No. 14 of the Report of that Committee is as follows:—

"That the electrical pressure at a temperature of 62° F. between the poles or electrodes of the voltaic cell known as Clark's cell may be taken as not differing from a pressure of 1·433 volt by more than an amount which will be determined by a Sub-Committee appointed to investigate the question, who will prepare a specification for the construction and use of the cell."

The following paper contains an account of some of the experiments made during the investigation.

In the same Report, Resolution 10 states that an unvarying current, which, when passed through a solution of nitrate of silver in water, in accordance with the specification attached to this report, deposits silver at the rate of 0·001118 of a gramme per second, may be taken as a current of 1 ampere.

The specification referred to is as follows:—

In the following specification the term silver voltameter means the arrangement of apparatus by means of which an electric current is passed through a solution of nitrate of silver in water. The silver voltameter measures the total electrical quantity which has passed during the time of the experiment, and by noting this time the time-average of the current, or if the current has been kept constant, the current itself can be deduced.

In employing the silver voltameter to measure currents of about 1 ampere the following arrangements should be adopted. The kathode on which the silver is to be deposited should take the form of a platinum bowl not less than 10 cm. in diameter, and from 4 to 5 cm. in depth.

The anode should be a plate of pure silver some 30 square cm. in area, and 2 or 3 millims. in thickness.

This is supported horizontally in the liquid near the top of the solution by a platinum wire passed through holes in the plate at opposite corners. To prevent the disintegrated silver which is formed on the anode from falling on to the kathode, the anode should be wrapped round with pure filter paper, secured at the back with sealing-wax.

The liquid should consist of a neutral solution of pure silver nitrate, containing about 15 parts by weight of the nitrate to 85 parts of water.

The resistance of the voltameter changes somewhat as the current passes. To prevent these changes having too great an effect on the current, some resistance, besides that of the voltameter, should be inserted in the circuit. The total metallic resistance of the circuit should not be less than 10 ohms.

Method of making a Measurement.

The platinum bowl is washed with nitric acid and distilled water, dried by heat, and then left to cool in a desiccator. When thoroughly dry it is weighed carefully.

It is nearly filled with the solution, and connected to the rest of the circuit by being placed on a clean copper support to which a binding screw is attached. This copper support must be insulated.

The anode is then immersed in the solution so as to be well covered by it and supported in that position; the connections to the rest of the circuit are made.

Contact is made at the key, noting the time of contact. The current is allowed to pass for not less than half-an-hour, and the time at which contact is broken is observed. Care must be taken that the clock used is keeping correct time during this interval.

The solution is now removed from the bowl, and the deposit is washed with distilled water and left to soak for at least six hours. It is then rinsed successively with distilled water and absolute alcohol, and dried in a hot-air bath at a temperature of about 160° C. After cooling in a desiccator it is weighed again. The gain in weight gives the silver deposited.

To find the current in amperes, this weight, expressed in grammes, must be divided by the number of seconds during which the current has been passed, and by ·001118.

The result will be the time-average of the current, if during the interval the current has varied.

In determining by this method the constant of an instrument the current should be kept as nearly constant as possible, and the readings of the instrument taken at frequent observed intervals of time. These observations give a curve from which the reading corresponding to the mean current (time-average of the current) can be found. The current, as calculated by the voltameter, corresponds to this reading.

In our experiments the method above described, which is that adopted by Lord Rayleigh, was carefully adhered to.

While our work was in progress, a paper on "The Causes of Variation of Clark Standard Cells" was communicated to the British Association by Mr. J. Swinburne ('Electrical Review,' August 28th, 1891). The results of our investigations confirm his conclusions in many respects.

In the first part of the paper we shall deal with the experiments on the absolute electromotive force of a Clark cell, and, in the second, with the comparisons between various cells and the conclusions to be drawn from them.

§ 2. *Theory of the Method.*

The theory of the method is very simple. A fairly constant current is passed through a silver voltameter and a known resistance. The value of the current is given by the voltameter, and from this the potential difference between the terminals of the resistance is found. This potential difference is compared by a potentiometer method with the E.M.F. of a Clark cell, and thus an absolute value is obtained for the E.M.F. of the cell.

We shall describe in turn the various parts of the apparatus and the method of experimenting.

§ 3. *The Standard Cell.*

Lord RAYLEIGH left at Cambridge, in the charge of one of us (R. T. G.), three of the cells he constructed during the year 1883. One of these has since dried up. The other two, which have been carefully kept, have been compared from time to time, and differ very slightly in E.M.F. (see Part II.). We took one of these, which we call Rayleigh No. 1, as our standard. Rayleigh No. 1 is a cell of the pattern originally adopted by LATIMER CLARK. According to the data in Lord RAYLEIGH's paper, "the saturated solution of zinc sulphate was nearly neutral. The metallic zinc was bought as pure from Messrs. HOPKIN and WILLIAMS. The mercurous sulphate was from the same source, and the metallic mercury was redistilled in the laboratory."

It seems probable that the cell Rayleigh No. 1, is No. 4 of Lord RAYLEIGH's paper, though it is difficult to be quite certain of this point. In his paper, 'Phil. Trans.,' 1885, Lord RAYLEIGH says: "Cells (4), (8), (9), were, I think, left at Cambridge." Of these it is clear ('Phil. Trans.,' 1884, p. 442), that No. 4 was of the original pattern, the others were made at a later date. Our cell, No. 1, is of the pattern originally devised by LATIMER CLARK, while No. 2 is of the form used later by Lord RAYLEIGH. We therefore infer that our No. 1 is Lord RAYLEIGH's No. 4.

In the earlier experiments, the E.M.F. of this cell was compared directly with the difference of potential between the ends of the resistance. As in this procedure there was some slight risk of passing an appreciable current through the cell, it was modified. A large cell, denoted in what follows by No. 90, or the bottle cell, was constructed in a glass bottle, and the E.M.F. of this was determined. This cell was from time to time compared with the standard.

§ 4. *The Voltameters.*

Five different platinum bowls were used.

I. The large bowl employed by Lord RAYLEIGH, in shape approximately the segment of a sphere, diameter across the top 10 cms., depth 4·5 cms.

II. A bowl, kindly lent us by Professor Liveing, 10 cms. in diameter, 3·5 cms. in depth, the bottom of this is flatter than that of I., and the sides more nearly vertical.

III. A bowl, very similar to I., and of about the same dimensions, also lent us by Professor Liveing.

IV. A third bowl, similar to I., and of about the same size, though much lighter, lent us by Mr. F. H. Neville.

V. A deep cup-shape bowl, 7·25 cms. in diameter, 8 cms. deep, belonging to the Laboratory.

Of these, No. II. had been used a good deal for chemical work. Its surface was somewhat dull, and we never succeeded in obtaining an adhesive deposit with it. Traces of the silver always came away in the washing, and when weighed, the silver was always less than that deposited in the other bowl. We have not used the deposits from this bowl.

In each experiment two bowls were used in series.

The anode was usually a circular piece of silver plate, about 7 or 8 cms. in diameter, and ·12 cm. in thickness, supplied by Messrs. Johnson and Matthey as "Ordinary Fine Silver Sheet," price 5*s.* per oz. This was supported horizontally in the liquid by three platinum wires, the whole being covered with filter paper secured at the back with sealing wax.

In the case of Bowl V., the anode was bent into the form of a cylinder, which was immersed in the liquid with its axis vertical.

The bowls rested on clean copper plates insulated on ebonite and paraffin blocks. The supports which carried the anodes were insulated in the same way. The insulation was tested by connecting up the voltameters before they had been filled with the liquid with a battery of six Leclanché cells and a delicate high-resistance galvanometer. No trace of a leak could be found.

The liquid used was a solution of silver nitrate, containing 85 parts by weight of distilled water and 15 parts of pure recrystallised silver nitrate, supplied by Messrs. Johnson and Sons, as containing 63·5 per cent. of fine silver, or 99$\frac{2}{3}$ per cent. of pure anhydrous nitrate of silver.

A coil of wire, having about the same resistance as two of the voltameters, was connected up in parallel with them, in such a way that, by means of a key consisting of mercury cups cut in a block of paraffin, the current could be sent either through the voltameters or through the coil. The adjustments were made with the current flowing through the wire, when all was complete the key was shifted so as to send the current through the voltameters, and the time taken.

§ 5. *The Standard Resistance.*

It was necessary that this should not be seriously heated by a current of about 1 ampere.

It was, therefore, constructed of a strip of platinoid about 1 cm. wide and ·05 cm. thick. This was wound on an open frame about 50 cms. long and 50 cms. wide by 6 cms. deep. The frame was of wood covered with strips of ebonite which insulated the metal from the wood.

The whole was immersed horizontally in a bath of paraffin, containing about 60 litres of oil. A stirrer, in the form of a T-shaped piece of wood, passed under the coil between it and the bottom of the bath, and by means of this the liquid could be kept in a state of agitation. This stirrer was worked frequently during an experiment. A delicate thermometer, placed with its bulb very close to the strip, showed an immediate slight rise in temperature, one or two tenths of a degree, if the oil was not stirred. If the stirring was maintained the rise during an experiment was usually only slight.

The ends of the platinoid strip were soldered to thick copper rods, which dipped into two mercury cups insulated on a paraffin block.

By means of copper rods, these cups could be put into communication with the B.A. bridge, and the resistance of the strip measured *in situ* in terms of the standard coil "Flat." This was done without shifting the coil both before and after each experiment; the two results never differed by more than ·0007 B.A. unit, and the mean has been taken in calculating the result. The resistance of the strip at 17° C. was 1·0011 B.A. unit.

For some of the experiments this resistance might, with advantage, have been higher, though the fact that it was nearly equal to the standard secured accuracy in the comparison with it, and it was thought desirable, from this point of view, to use the same resistance throughout.

In order to reduce the effects due to variations in the resistance of the voltameters, a resistance of thick platinoid wire, usually some twelve or fifteen ohms in amount, was included in the circuit. This was varied until the current was of the right amount.

§ 6. *The Balance.*

A short beam balance by OERTLING was used for the weighings. This and the weights were the same as those employed in the determination of the specific resistance of mercury by GLAZEBROOK and FITZPATRICK ('Phil. Trans.,' A., 1888). The weights had been compared with the standard, and the correction found to be inappreciable. Some of the weighings were done in both pans in order to determine the ratio of the arms of the beam. This was found to be 1·00002. The correction to the weight *in vacuo* varied between 1·000030 and 1 − ·000013, according to the number of platinum weights used; both these are too small to affect our results, and have not been introduced into the calculations.

§ 7. *The Clock.*

The Laboratory chronometer, beating half-seconds, was used to give the time during which the current flowed, and the rate of the chronometer was determined by a series of comparisons with a clock belonging to the Cambridge Philosophical Society, which is rated from the Observatory.

It was found that the chronometer was losing at the rate of about ·16 seconds per hour. A small correction for this has been introduced in the final result.

§ 8. *The Resistance Boxes and Apparatus for the Comparison of Electromotive Forces.*

For the comparison of the electromotive forces two resistance boxes by ELLIOTT BROS. were used. The coils in these boxes agreed together sufficiently nearly to introduce no serious error. The current from two Leclanché cells ran continuously through 10,000 ohms, taken out of the two boxes in series. The standard Clark or the bottle cell was connected with one of the boxes through a sensitive galvanometer and a resistance coil of 10,000 ohms, and plugs transferred from one box to the other until there was no deflection on closing the galvanometer circuit. The Leclanchés remained very steady during the whole course of the experiments. The resistance required in the main circuit to balance the Clark changed in about a fortnight from 5722 to 5784, or about 1 per cent. This comparison was made from time to time during each individual experiment, to check the constancy of the Leclanchés, with satisfactory results. On August 7 an extreme variation of 6 ohms occurred. On other occasions the change during the time an experiment lasted was only 2 or 3 ohms. In making the reductions the mean value was taken.

The galvanometer, battery, and resistance boxes were all insulated on separate paraffin blocks.

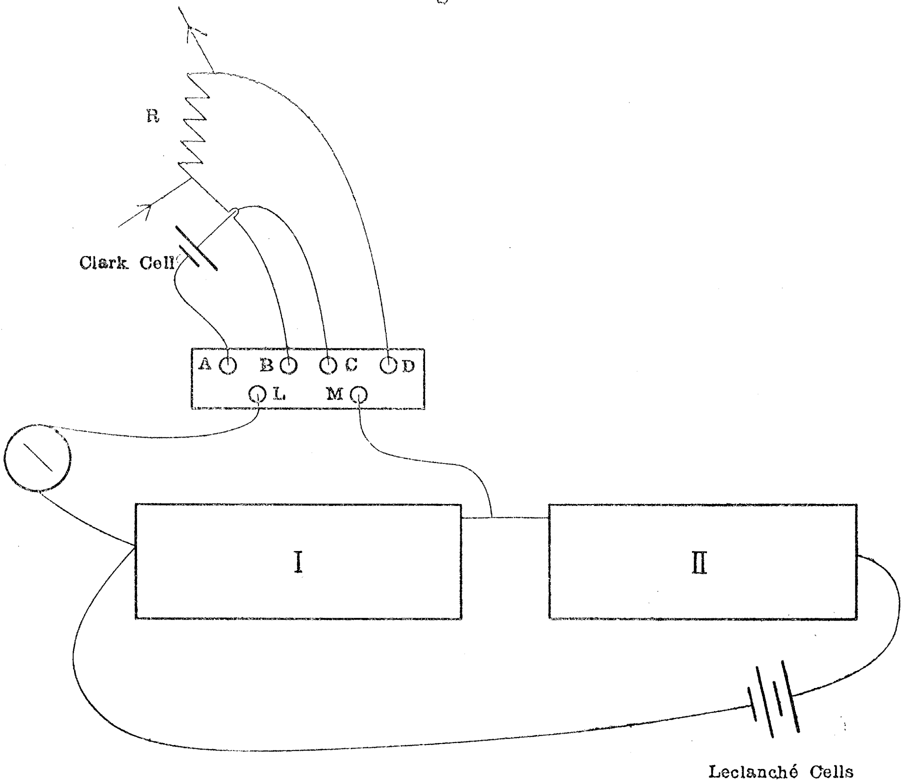
The temperature of the bath containing the Clark was observed from time to time during the experiments. It usually rose slightly by about 0°·1 C.

The thermometers employed had been tested at Kew, and the necessary corrections are introduced.

Fig. 1 gives a diagrammatic representation of this part of the apparatus; I. and II. are the two resistance boxes through which the current from the two Leclanchés passes.

A, B, C, D, L, M are six mercury cups in a block of paraffin. Of these L is connected through the galvanometer G with one end of the box I., while M is in connection with the junction of the two boxes. The poles of the Clark are connected to A and C, and well insulated wires join B and D to the ends of the strip resistance R. Connections can be made as needed among the cups by means of pieces of wire bent into the required form and attached to pieces of sealing wax as insulating handles. When a current, i, is maintained in the resistance R, the difference of potential between B and D is Ri. By connecting L to B and M to D, and adjusting the plugs in I. and II., keeping their sum constant until there was no deflection of the galvanometer, this difference of potential was expressed in terms of the E.M.F. of the Leclanchés, while by connecting A to L and C to M the ratio between the E.M.F. of the Clark and that of the Leclanchés was found. This method was adopted in some of the experiments. In other experiments, C and D were connected together, while A was joined to L and B to M. In this arrangement, the electromotive force between A and B was the difference between that of the Clark and Ri. The difference was expressed in terms of the Leclanchés, and then compared as before with that of the Clark. By employing a proper current in the main circuit through the voltameters, the difference between the E.M.F. of the Clark and Ri could be made small, and thus the result was more nearly independent of changes in the Leclanchés.

Fig. 1.



The sensitiveness of the galvanometer was such that an alteration of the resistance in I. by 1 ohm produced a deflection of about 3 cms. on the scale, this corresponds to a variation in the E.M.F. between L and M of about one six-thousandth of a Clark cell. Thus variations of ·0001 volt could be detected without difficulty.

§ 9. *Details of the Method.*

The theory of the experiment just outlined supposes that the current i in the main circuit remains constant. In practice this is not the case; two methods were adopted for meeting the difficulty.

Let V be the resistance taken out of the Box I. when the ends of the resistance R are connected to L and M. Then as the current varies V varies also, being always proportional to i. During the time the current was passing a series of observations of the value of V, regulated to produce a balance, was made and the corresponding times noted. These observations were plotted on squared paper, and a curve formed with the times for abscissæ and the values of V for ordinates; the area of this curve is proportional to the quantity of electricity which has passed, and it is easy to calculate from the curve the mean value of the current and the corresponding value of V. This method was followed in the observations on July 31, August 5, and August 7.

On July 31 the value of V changed considerably, viz., from 3876 to 3917·5. With one exception, however, the observations lie on a very regular curve, and the mean value, 3904·5, got from the curve is probably accurate to 1 or 2 ohms.

On August 5 the changes were very small, and, as shown by the corresponding curve for the Clark cells, are almost entirely due to alterations in the Leclanché cells. The curves are given in Plate 16, figs. 1, 2, 3.

In all the other experiments an adjustable mercury resistance was introduced into the main circuit with the voltameters. The plugs in the boxes were adjusted until on making the galvanometer key there was no deflection. The galvanometer circuit was then kept closed, and the mercury resistance adjusted so that no deflection should take place. Occasionally it happened that the changes needed in the resistance of the main circuit to maintain i constant were outside the limits of the mercury rheostat. When this was the case a suitable change was made in the plugs in I. and II. and in the rheostat simultaneously, and the time noted. The change needed, except on the morning of August 12, was always small, some 4 or 5 ohms at most, and the mean value of V was readily determined with all the accuracy required. On August 12, after the current had been flowing steadily for 25 minutes, a sudden drop of over 1 per cent. took place. As during the next five minutes the current continued somewhat unsteady, the experiment was concluded at the end of 30 minutes 45 seconds, a much shorter time than in any of the other experiments.

In this second method of making the observations the very slight heating effect produced in the strip coil when the bath was not stirred was just observable. A balance was obtained, the bath being unstirred for a few moments. On moving the stirrer the spot was very slightly deflected in the direction indicating a fall in the resistance R, and the rheostat required a slight readjustment to restore the balance. The readjustment necessary, however, was extremely slight, being equivalent to a change of only a small fraction of an ohm in the Box I. As 1 ohm in the box means an alteration of ·00024 volt in the E.M.F., the error produced by heating in the strip was quite negligible.

§ 10. *Method of Carrying out an Experiment.*

The usual method of conducting the observations was as follows:—

The platinum bowls were washed with nitric acid and distilled water, dried by heating in a gas flame, and left to cool, usually overnight, in a desiccator. They were then weighed and placed in position, being filled with the solution, the anodes were immersed and the necessary connections made; while this was being done the current was allowed to flow in the main circuit through the alternative wire, and the value of the resistances required in the boxes to balance the Clark and the potential difference then existing between the ends of the strip coil approximately determined.

In cases in which the bottle cell No. 90 was used the difference between its E.M.F. and that of the standard Rayleigh No. 1 was found by the usual opposition method.

The main current was then broken and the difference in resistance between the strip coil and the standard "Flat" determined by CAREY-FOSTER's method, the necessary temperatures being observed.

The main current was then made, still through the alternative wire, and the resistances in the boxes required to balance the Clark accurately taken. The plugs were then set to the approximate value required to balance the potential difference between the ends of the strip coil, and the key in the main circuit shifted so as to send the current through the voltameters, the time being noted on the chronometer. Some small changes in the resistance boxes or in the mercury rheostat were usually required to obtain a balance in the galvanometer circuit. These were made and the spot of light watched, as already described, the necessary changes being made from time to time to keep it at rest.

After the experiment had proceeded for some time a comparison between the Clark and Leclanchés was usually again made as rapidly as possible. This was done by shifting the connections from L and M into the cups A and C, the current in the main circuit not being interfered with. The connections were again restored to their original position and the experiment proceeded as before. After the current had passed for some time, usually from forty minutes to an hour, it was again broken, the time being noted.

A comparison between the Clark and the Leclanchés was again made, and the differences between the electromotive forces of the bottle cell No. 90 and the standard and between the resistances of the strip coil and flat were observed.

The temperatures of the bath containing the strip coil and of the bottle and standard cells were noted from time to time during the experiment.

While the comparisons of E.M.F. and of resistance were in progress the bowls were rinsed with distilled water and then left to soak overnight in distilled water. The next morning they were again rinsed with distilled water and alcohol and then dried in a hot air bath, at a temperature of from 160° to 180° C.

After cooling for some hours in a desiccator they were weighed. The weighings were repeated on the following day, the bowls having usually been left for the interval in the balance case. In some cases during the interval the bowls were again heated. In none of the observations was there any difference sufficient to affect the result between the weighings.

Temperature corrections had to be introduced into the comparison between the bottle cell and the standard, for these could not conveniently be put into the same bath, and consequently differed slightly in temperature.

This was done by the aid of Lord RAYLEIGH's value for the coefficient, viz., ·00078—a value which our own experiments (see p. 615) sufficiently confirmed—in the following way. Since the plugs required out of the Box I. to balance the Clark were about 5800 ohms, a change of ·00078 in the E.M.F. of the Clark will mean a change in the resistance of 5800 × ·00078, or about 4·5 ohms in the box. Thus an increase of 1° in the temperature of the cell means a fall of 4·5 ohms in the resistance required to balance it. The actual change in E.M.F. corresponding to this will be 1·43 × ·00078, or ·00112 volt, and the change corresponding to one ohm of the box is found by dividing this by 4·5. This gives ·00025 volt.

The temperature of the bottle cell and of the Leclanchés varied slightly during the progress of each experiment, and part of the variations observed in the ratios of the two are no doubt due to temperature changes.

§ 11. *Details of Experiments.*

We proceed now to the details of each experiment. Most of these can be best given in tabular form, and this is done in Table I. (p. 581).

Some explanation is needed, however, of the method by which the values of some of the tabulated numbers, specially those in columns 3, 6, 10, and 15, are arrived at, and of the notation employed.

Let V be the resistance out of the box required to balance the difference of potential Ri between the ends of the strip coil, W that required to balance the Clark, E the E.M.F. of the Clark which was compared with Ri at the temperature of the observation.

R is, as above, the resistance of the strip, i the current. Let M be the mass of silver deposited, T the time the current has passed, and γ the electrochemical equivalent of silver in grammes per ampere per second.

Then

$$\gamma = \cdot 001118.$$

Then we have

$$M = i\gamma T,$$

$$E/Ri = W/V,$$

therefore,

$$E = R \,.\, \frac{W}{V} \cdot \frac{M}{\gamma \,.\, T}.$$

The values of E thus found require correcting (1) to reduce them to a common temperature of 15° C. (2) for the difference between the bottle cell and the standard Rayleigh 1.

Experiment 1, July 31, 1891.

The observed values of V and W are shown on Plate 16. In these one vertical division represents 5 ohms, and one horizontal division 5 minutes. The curves from which the numbers were calculated were drawn to a larger scale. It will be seen that the value of i, as indicated by the values of V, rose gradually for about 25 minutes, then remained fairly steady for about 15 minutes, and afterwards began to fall. The mean value for V, calculated as already described, is 3875 + 29·5, or 3904·5.

Three observations were taken for W; the mean value is 5722·5. Bowls I. and II. were used.

Experiment 2, August 3, 1891.

The observations are given in Plate 16. The current remained fairly steady for about 25 minutes, then suddenly increased considerably, the resistance changing in five minutes from 4585 to 4600, dropping in the next 15 minutes to 4595. The mean value of V is 4591 ohms, while that of W is 5756·5. Bowls I. and II. were used.

After these two experiments precautions were taken to work only when no other electrical work was going on in the laboratory. The current was supplied from storage cells in the battery room of the laboratory, and the wires conveying the current into the room in which the experiment was conducted were not satisfactorily insulated from other wires conveying a current from other cells into a different room. Fluctuations in the current were caused when these other cells were working.

Experiment 3, August 5.

The curves are shown in Plate 16. It will be seen that the variations are much less; in fact, the curves for V and W are very approximately parallel straight lines, showing that the changes are almost entirely due to the alterations in the Leclanchés. The mean values are—

$$V = 3691{\cdot}2,$$
$$W = 5751{\cdot}5.$$

Bowls I. and II. used.

In each of these three experiments some of the deposit in Bowl No. II. was lost in the washing, and the results from this bowl have not been used.

After this the mercury rheostat was used. This consists of two parallel grooves in a piece of dry mahogany which were filled with mercury. A movable copper bridge put the two columns into electrical connection. The current entered at one end of one column, passed along it, and after traversing the bridge emerged from the similar end of the second column. By sliding the bridge, the length of column traversed by the current was varied. A scale of centimetres was fitted parallel to the grooves, and it was found that with a current of about 1 ampere, shifting the bridge by 50 divisions of the scale produced an alteration in the current, which required a change of 1 ohm in the Box No. 1 to balance it; in other words, the difference of potential between the ends of the strip coil was changed by ·00025 volt, and the current by about ·00025 ampere.

Experiment 4, August 7.

Values for W 5773, 5775, 5770; mean, 5772·5. The difference between the E.M.F. of the Clark and R*i* was observed, and the resistance out, which was 2149, remained unchanged.

Thus

$$W - V = 2149,$$

therefore

$$V = 3623{\cdot}5.$$

The slide of the rheostat was moved over only about 10 divisions, so that the current was very constant. Bowls I. and II. used.

Experiment 5, August 10.

In this experiment a very large current, about 1·6 ampere, was used. The silver was deposited in four bowls, Nos. I. and IV. being arranged in parallel and then in series with them, Nos. III. and V. also in parallel. The value of W remained steady at 5784, and the value of W — V was also steady. By an oversight the plugs out for W — V were not noted till after the experiment was concluded. They lay certainly between 220 and 225, but there is some doubt as to the exact unit; we incline to think it was 223. With this value we have

$$V = 5561.$$

The slide was shifted about 24 divisions, so that the variation in the current was small.

Experiment 6, August 12, morning.

The value of W varied from 5756 to 5754; mean W = 5755. The value of W — V remained steady at 1176 for 25 minutes, when a sudden change took place. The main current was stopped, the time being noted on the chronometer, and the plugs altered to 1238. The current was again started, the time being taken, and remained fairly steady for 2·5 minutes, when the plugs were altered to 1233 without breaking the main current, and the slide correspondingly adjusted. The current remained steady for a time, but at the end of 3·25 minutes more showed signs of variation, so the experiment was ended and the time taken.

The current lasted, in the first instance, for 25 minutes, and in the second, for 5 minutes 45 seconds, thus we have for T the value 1845 seconds.

The value of W − V was 1176 for 25 minutes, 1238 for 2·5 minutes, and 1233 for 3·25 minutes.

From these we obtain, as the mean value of W − V, 1187, and hence V = 4568.

The fact that there was a break in the middle so that four readings of the chronometer are involved, renders the time measurement less trustworthy than in the other experiments.

Bowls I. and IV. were used.

Experiment 7, August 12, afternoon.

W changed from 5753 to 5756 during the experiment, the mean value was 5754·5. The value of W − V was changed after the current had been passing for 5 minutes from 3349 to 3344, but without breaking the current, the slide being readjusted to suit. It remained very steady at this value while the experiment lasted. The whole time of the experiment was 50 minutes 5 seconds.

Thus the mean value of W − V is 3344·5, therefore

$$V = 2410.$$

Bowls III. and V. were used.

Experiment 8, August 14, morning.

The value of W changed from 5738 to 5737; mean value, 5737·5. The value of W − V was steady all the time at 1120, and the slide was very little altered; thus the current was very steady, and we have

$$V = 4617·5.$$

Bowls I. and IV. were used.

Experiment 9, August 14, afternoon.

The value of W changed from 5730 to 5729·5; mean value, 5729·8. The current ran for 1 hour and 5 seconds.

The values of W − V were 3290 for 6 minutes, then 3288 for 26 minutes, changing during the next minute to 3280, and after that being steady at 3280; for the remaining 27 minutes the current was not broken, but the slide of the rheostat was altered as the resistances were changed. From this we have as the mean value of W − V, 3284·5, whence

$$V = 2445·3.$$

Bowls III. and V. were used.

It should be noticed, in the cases in which the current varied, that an accurate value of the time at which the changes in the position of the slide took place, is not needed, provided the whole time is known accurately.

These are all the experiments made.

TABLE I.

1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16
No. of experiment.	Date.	Value of R, resistance of strip.	Temp. R.	Value of W.	Value of V.	Temp. of Clark.	Mass of silver in first bowl.	Mass of silver in second bowl.	Value of M adopted.	Value of T, time of flow.	Value of E at temperature of Clark.	Correction to 15°.	Value of E at 15°.	Corrections to Rayleigh 1.	E.M.F. of Rayleigh 1., at 15°.
1	July 31 .	·9877	17°	5722·5	3904·5	16·5	2·6071	*2·6003**	2·6071	2357	1·4322	·0019	1·4341	0	1·4341
2	Aug. 3 .	·9877	17	5756·5	4591	16·4	3·2070	*3·2043**	3·2070	2480	1·4320	·0016	1·4336	0	1·4336
3	Aug. 5 .	·9877	17	5751·5	3691·2	16·45	2·8095	*2·8031**	2·8095	2700	1·4325	·0016	1·4341	0	1·4341
4	Aug. 7 .	·9877	17	5772·5	3623·5	17	2·7935	*2·7905**	2·7935	2745	1·4323	·0022	1·4345	—·0005	1·4340
5	Aug. 10	·9878	17·4	5784	5561	16·5	4·6951	4·6926	4·6939	3010	1·4328	·0017	1·4345	—·0005	1·4340
6	Aug. 12 morning	·9879	17·9	5755	4568	17	2·3745	2·3732	2·3739	1845	1·4325	·0022	1·4347	—·0005	1·4342
7	Aug. 12 afternoon	·9880	18·1	5754·5	2410	17·3	2·0399	2·0385	2·0392	3005	1·4321	·0026	1·4347	—·0005	1·4342
8	Aug. 14 morning	·9882	18·7	5737·5	4617·5	17·8	3·9104	3·9104	3·9104	3000	1·4316	·0031	1·4347	—·0007	1·4340
9	Aug. 14 afternoon	·9883	19·2	5729·5	2445·3	18·3	2·4908	2·4924	2·4916	3605	1·4318	·0036	1·4354	—·0009	1·4345

* In all these observations Bowl II. was used and some silver was visibly lost in the washing. The numbers therefore have not been employed.

§ 12. *Discussion of Results.*

The mean of the above values is 1·4341 volt at 15° C. The variation from the mean is small. The smaller result in Experiment 2 may be due to the unsteadiness of the current during the experiment. It will be remembered it rose in value suddenly by about one part in 300 during the observations. The result in Experiment 9 is too high. This is, no doubt, due to the fact that the temperature of the bottle cell was varying somewhat. The temperature of the bath changed between the morning and afternoon observations on August 14 by 0°·5 C. Now, our observations have shown us that the E.M.F. of the cell lags behind the temperature when this is changing. This lag is due to the time taken in changing the state of concentration of the zinc sulphate solution. It is practically certain that on the afternoon of August 14 the cell had not reached the steady state corresponding to 18°·3, and that, therefore, the correction to 15° of ·0036 volt is too high.

It will be remembered that some uncertainty of one or two units is attached to the value of V in Experiment 5, August 10.

The weighings of the second bowl, No. 2, in Experiments 1, 2, 3, 4 have not been used because some small amount of silver was visibly lost in the washings.

The weighings in the other experiments agree with each other by about one part in 2000. This agreement is rather less good than that attained in Lord Rayleigh's experiments. It must be remembered that the rate of deposition was about three times as great as in his work, and this affects the deposit. The value of the E.M.F. thus found needs increasing by about one part in 20,000 for the error of the clock, and we thus obtain as the E.M.F. of the standard cell, Rayleigh No. 1, at a temperature of 15° C. the value

1·4342 volt.

The English standard legal temperature is 62° Fahr., or $16\frac{2}{3}$° C.
Reducing to this temperature we find the value

1·4324 volt at 62° Fahr.

The value found by Lord Rayleigh for his standard No. 1, was 1·435 volt at 15°, if we include another figure, the value given in Lord Rayleigh's Table becomes 1·4348. Now, his cell No. 4, which is probably our No. 1, was two parts in 10,000 below his No. 1; and again we have, in accordance with the resolution of the Board of Trade Committee, taken ·9866 as the value of the B.A. unit in ohms, Lord Rayleigh used ·9867. On this account our result needs to be raised by one part in 10,000 to compare with his; thus altogether our result needs to be raised by three parts in 10,000, or by about ·0004 volt, to give the E.M.F. of his original cell, No. 1, in his units. We thus get for this cell the value 1·4346 volt, as against 1·4348 found by Lord Rayleigh, and the agreement is within the errors of the observations.

A reference to the table shows that our bottle cell No. 90 is about three parts in 10,000 above the cell Rayleigh 1. It agrees more nearly, therefore, with Lord Rayleigh's original standard.

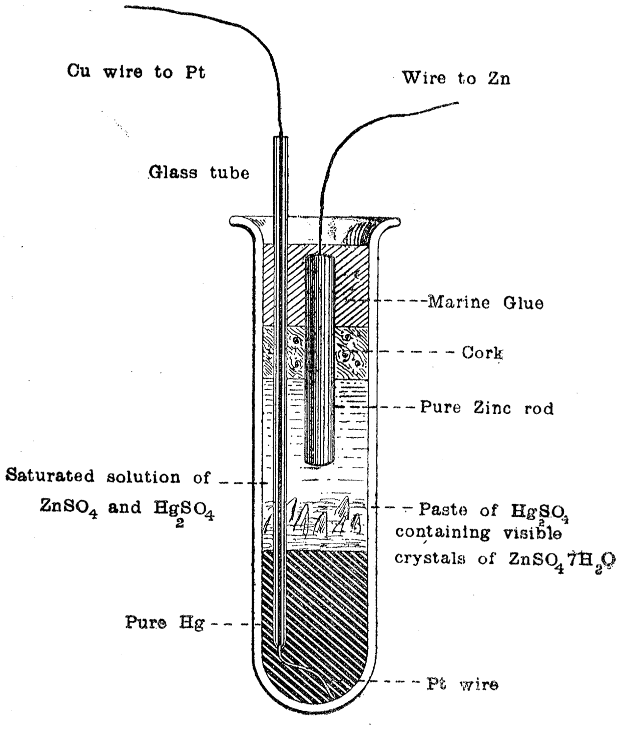
In comparing our result with that of other experimenters it must be remarked that it is given in "volts." To reduce it to the "legal volts" of the Paris Congress it must be multiplied by the ratio 1063/1060, and it then becomes at 15° C. 1·4382 "legal volt."

Part II.—Comparison of Various forms of Cells and of the Materials used.

§ 13. *Introduction. General Remarks. Methods of Testing.*

A normal Clark cell is one prepared according to certain definite directions, and the electromotive force of such a cell has been determined in Part I. above. Various causes may lead to a deviation from the normal value for the E.M.F. of any given cell, and it becomes important to consider these. We have in the course of the work met with at least one batch of cells which agree very closely among themselves, but which differ very considerably in E.M.F. from the standard. Directions for the construction of a normal Clark cell have been provisionally drawn up by a sub-committee of the Electrical Standards Committee of the Board of Trade, and have been issued to various laboratories for the purpose of gaining experience and enabling the Committee to issue at some future date a definite memorandum. These instructions in

Fig. 2.



their latest form, June 23, 1891, are given here. Fig. 2 shows the arrangements of the parts of the cell as described in the memorandum.

Memorandum on the Preparation of the Clark's Standard Cell.

Definition of the Cell.

The cell consists of zinc and mercury in a saturated solution of zinc sulphate and mercurous sulphate in water, prepared with mercurous sulphate in excess, and is conveniently contained in a cylindrical glass vessel.

Preparation of the Materials.

1. *The Mercury.*—To secure purity it should be first treated with acid in the usual manner, and subsequently distilled in vacuo.

2. *The Zinc.*—Take a portion of a rod of pure zinc, solder to one end a piece of copper wire, clean the whole with glass paper, carefully removing any loose pieces of the zinc. Just before making up the cell dip the zinc into dilute sulphuric acid, wash with distilled water, and dry with a clean cloth or filter paper.

3. *The Zinc Sulphate Solution.*—Prepare a saturated solution of pure ("pure re-crystallised") zinc sulphate by mixing in a flask distilled water with nearly twice its weight of crystals of pure zinc sulphate, and adding a little zinc carbonate to neutralise any free acid. The whole of the crystals should be dissolved with the aid of gentle heat, *i.e.*, not exceeding a temperature of 30° C., and the solution filtered, while still warm, into a stock bottle. Crystals should form as it cools.

4. *The Mercurous Sulphate.*—Take mercurous sulphate, purchased as pure, and wash it thoroughly with cold distilled water by agitation in a bottle; drain off the water, and repeat the process at least twice. After the last washing drain off as much of the water as possible.

Mix the washed mercurous sulphate with the zinc sulphate solution, adding sufficient crystals of zinc sulphate from the stock bottle to ensure saturation, and a small quantity of pure mercury. Shake these up well together to form a paste of the consistence of cream. Heat the paste sufficiently to dissolve the crystals, but not above a temperature of 30°. Keep the paste for an hour at this temperature, agitating it from time to time, then allow it to cool. Crystals of zinc sulphate should then be distinctly visible throughout the mass; if this is not the case, add more crystals from the stock bottle, and repeat the process.

This method ensures the formation of a saturated solution of zinc and mercurous sulphates in water.

The presence of the free mercury throughout the paste preserves the basicity of the salt, and is of the utmost importance.

Contact is made with the mercury by means of a platinum wire about No. 22 gauge. This is protected from contact with the other materials of the cell by being sealed into a glass tube. The ends of the wire project from the ends of the tube; one end forms the terminal, the other end and a portion of the glass tube dip into the mercury.

To set up the Cell.

The cell may conveniently be set up in a small test tube of about 2 cm. diameter, and 6 or 7 cm. deep. Place the mercury in the bottom of this tube, filling it to a depth of, say, 1·5 cm. Cut a cork about ·5 cm. thick to fit the tube; at one side of the cork bore a hole through which the zinc rod can pass tightly; at the other side bore another hole for the glass tube which covers the platinum wire; at the edge of the cork cut a nick through which the air can pass when the cork is pushed into the tube. Pass the zinc rod about 1 cm. through the cork.

Clean the glass tube and platinum wire carefully, then heat the exposed end of the platinum red hot and insert it in the mercury in the test tube, taking care that the whole of the exposed platinum is covered.

Shake up the paste and introduce it without contact with the upper part of the walls of the test tube, filling the tube above the mercury to a depth of rather more than 2 cm.

Then insert the cork and zinc rod, passing the glass tube through the hole prepared for it. Push the cork gently down until its lower surface is nearly in contact with the liquid. The air will thus be nearly all expelled, and the cell should be left in this condition for at least 24 hours before sealing, which should be done as follows.

Melt some marine glue until it is fluid enough to pour by its own weight, and pour it into the tes tube above the cork, using sufficient to cover completely the zinc and soldering. The glass tube should project above the top of the marine glue.

The cell thus set up may be mounted in any desirable manner. It is convenient to arrange the mounting so that the cell may be immersed in a water bath up to the level of, say, the upper surface of the cork. Its temperature can then be determined more accurately than is possible when the cell is in air.

It is clearly desirable to determine whether these instructions are sufficient to enable different makers to produce cells having the same E.M.F., and to investigate in what points a slight departure from the instructions may be made without materially affecting the E.M.F. of the cell.

The following paper contains an attempt to answer the questions :—

(1.) How far cells made with different samples of materials have the same E.M.F. ?

(2.) How far batches of cells from different makers agree with our standard ?

(3.) What are the chief sources of variation in a Clark cell ?

We have examined over 100 cells, of which we shall now give the details.

The values have generally been given in terms of the cell No. 1, constructed by Lord RAYLEIGH over eight years ago.

The constancy of this cell has been ascertained by comparison with other standards, and by the fact that it was our ultimate standard of reference for the absolute value of the E.M.F. in the investigation already described. The result of this agrees almost exactly with Lord RAYLEIGH'S.

The method of comparison already described in Part I. has been employed in all the later comparisons. Two Leclanché cells are allowed to work through two resistance boxes, with a total resistance of 10,000 ohms, in circuit. One of the Clarks, usually the bottle cell, is connected through a galvanometer and a high resistance to two points on this circuit, and the resistances adjusted until the potential difference between these points just balances the E.M.F. of the Clark. This Clark is then connected in turn in opposition with the other cells of which the E.M.F. is required, and the difference between the electromotive forces of the two determined in terms of the fall of potential along the Leclanché circuit.

We found that this fall of potential changed very slightly throughout our experiments. The fall corresponding to 1 ohm is very approximately ·00025 volt, and we have expressed the differences between the various cells examined in terms of this unit. We will collect, in a series of Tables, the results obtained, together with descriptions of the method of construction.

§ 14. *Tests on various Cells used as Standards. Cells set up by Lord* RAYLEIGH, *Dr.* SCHUSTER, *Mr.* ELDER, *and Mr.* CALLENDAR.

Table II. refers to cells of which most were not made by ourselves, but which have either been in the Laboratory for some time or have been lent us by other makers.

In some cases comparisons of an early date made by other experimenters have been included. In such cases the standard used is not always quite definite, but details will be given. We proceed to describe the cells.

Cell No. 1.—This is our standard cell, made in 1883 by Lord RAYLEIGH, probably the No. 4 of his paper, 'Phil. Trans.,' 1884: "It was prepared generally according to directions given by Dr. ALDER WRIGHT ('Phil. Mag.,' July, 1883). The saturated solution of zinc sulphate was nearly neutral. The metallic zinc was bought as pure from Messrs. HOPKIN and WILLIAMS. The mercurous sulphate was from the same source, and the mercury was re-distilled in the laboratory."

Cell No. 2.—Two other cells, probably Nos. 8 and 9 of Lord RAYLEIGH's paper, were left by him in Cambridge. They were set up in January, 1884. One of these has since dried up, the other is our Cell No. 2. The same materials as for the Cell No. 1 were used. According to Lord RAYLEIGH's tests, when first made, they were slightly higher—by some two or three of our units, than our Cell No. 1.

Cells Nos. 3*a*, 3, 4, 5.—These are cells of the H form suggested by Lord RAYLEIGH, made in 1886, at Wellington College, by Mr. H. M. ELDER. Originally there were five cells; the other has been destroyed through the bursting of the tube containing the zinc amalgam. They were prepared according to the descriptions given by Lord RAYLEIGH in his paper, from materials obtained from various sources, and when tested soon after being made, were fairly close to his standard.

The first set of comparisons quoted were made by Mr. E. H. GRIFFITHS, who, at the same date, tested the Rayleigh cells Nos. 1 and 2.

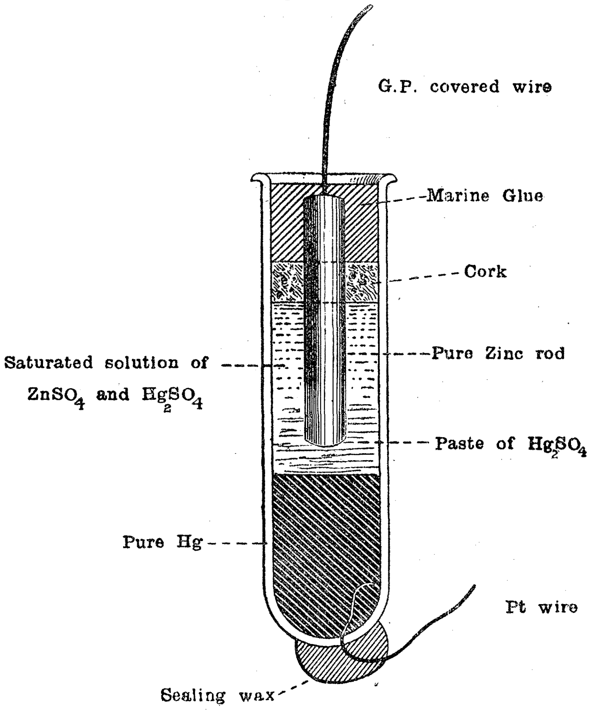
Cells Nos. 6, 7, 8, 9, 10, are five cells made in 1886, by Mr. H. L. CALLENDAR, marked by him as I., II., III., IV., V. They are of the pattern described by Lord RAYLEIGH in his Second Paper, 'Phil. Trans.,' 1885. It will be convenient to quote here his directions, as they will be frequently referred to.

"The zinc sulphate is prepared in a flask by mixing distilled water with about twice its weight of crystals. A little carbonate of zinc is added to neutralize the free acid, and the solution is effected with the aid of *gentle heat.* If time can be afforded, it is a good plan to let the solution stand, as a good deal of iron is usually deposited, even when 'pure' zinc sulphate is used. The solution may then be filtered in a warm place, into the stock-bottle.

"When it is intended to charge H cells, or to prepare paste, the bottle should be exposed to gentle warmth for a few hours, and the solution drawn with a pipette from near the crystals at *the bottom of the bottle.* Otherwise there is no security that the liquid used will be saturated.

"To prepare paste we may rub up together in a mortar 150 grms. mercurous sulphate, as purchased, 5 grms. zinc carbonate, and as much of the saturated solution as is required to make a thick paste. Carbonic anhydride is liberated, and must be allowed a sufficient time to separate. I have found it convenient to leave the paste in a mortar for two or three days, rubbing it up at intervals with additions of the zinc sulphate solution, until the gas has escaped. By the addition of a small crystal, and by evaporation, we have security that the paste is saturated, and will remain so, notwithstanding such moderate elevation of temperature as the cells are expected to bear. The paste may then be transferred to a tightly corked bottle, and, so far as my experience extends, will remain available for many months at least. Before pouring the bottle of paste should be well shaken up."

Fig. 3.



The cell takes the form of a small tube with the platinum wire sealed in at its lower end. (See fig. 3.) "In charging the cells the first step is to pour in sufficient *pure* mercury to cover the platinum effectively. The paste is introduced with the aid of a small funnel, care being taken not to soil the sides above the proper level. The rods, cut from rods of pure zinc, as supplied by HOPKIN and WILLIAMS and not re-cast, are soldered to copper wires and cleaned in the lathe. Just before use they are dipped in dilute sulphuric acid, washed in distilled water, and dried with a clean cloth or filter paper. Each zinc is mounted in a short piece of cork fitting the tube (but not too tightly) and nicked in order to allow of the passage of air. The cork is pushed gradually down until its lower face is almost in contact with the paste. The object is to leave but little air, and at the same time to avoid squeezing up the paste between the cork and the glass. The whole is now made tight by pouring marine glue over the cork, high enough to cover the zinc and soldering and leave only the wire projecting. The tube should rise high enough to receive the glue and thus secure a good adhesion.

In the operation of pouring in the marine glue the glass is heated by the glue sufficiently for adhesion; but this heat does not extend appreciably below the cork.

Neither in this nor in any other stage of the process of charging is heat applied to the paste."

Mr. CALLENDAR'S cells were prepared in this way, except that the zinc sulphate solution was boiled with zinc oxide. Lord RAYLEIGH recommends the use of "gentle heat," not boiling. The area of the zinc immersed is various in the different cells, being small in No. 6, large in Nos. 9 and 8. These cells have always been very close to the standard. They were compared with the standard No. 1 by Mr. GRIFFITHS, in August, 1890. In February, 1891, they were taken to London and compared there with the cells in the possession of the Board of Trade.

Cell No. 90.—This is a large cell made in a wide-mouthed bottle, about 10 cm. high and 7 or 8 cm. in diameter, by one of us (S. S.) in July, 1891. The paste was prepared according to the Board of Trade memorandum, and is the same as that used in cells Nos. 71–79. (See later, p. 603.)

The zinc was ordinary commercial plate zinc not amalgamated. At first the cell was too high by 25 of our units; crystals of zinc sulphate were dropped in on July 9, and on July 10 it was 14 units too high. From this date onwards the tests are given in the Table.

Cell No. 97.—A large cell set up by Professor SCHUSTER, and brought by R.T.G. from Manchester, on July 11. The cell is set up in a kind of small WOULFE'S bottle about 5 cm. across, and some 7 or 8 cm. high. The central opening at the top contains a thermometer; the zinc and platinum pass in glass tubes through the other openings, being secured with sealing wax into glass tubes. There is also a mercury valve which permits of the escape of gas if any is evolved.

Dr. SCHUSTER writes as follows of the cell:—"The cell was made with mercurous sulphate prepared and treated as follows:—Mercurous nitrate was prepared by dissolving mercury in nitric acid and boiling up the solution thus formed with mercury in a flat-bottomed flask, the mercury completely covering the bottom of the flask. The salt was crystallised out from the solution and dried with filter paper. The mercurous nitrate was then dissolved in an 8 per. cent. solution of nitric acid and precipitated with sodium sulphate. The precipitate was filtered, washed, and strained by pressure, then once washed with a saturated solution of zinc sulphate. The sulphate was then boiled for half-an-hour in a conical flat-bottomed flask containing enough mercury to cover the bottom, some zinc sulphate solution and crystals being added before treating; the mercurous sulphate was then transferred directly to the cells, the E.M.F. directly after setting up (April 30) was -28, the unit being 10^{-4}

of a Clark cell. On May 5, it was − 12, and on May 25, ± 0, the standard being an old carefully prepared small cell agreeing closely with a number of other cells. About a dozen comparisons were made between the end of May and July 11, and it was within a few parts in 10,000 of the standard always."

These last two cells could be immersed in a water bath, and were always so used, side by side. The two Rayleigh cells Nos. 1 and 2, were enclosed in two large test tubes, and these were immersed in water. In some of the earlier experiments they could not conveniently be put into the same bath as Nos. 90 and 97; in the later experiments the four cells were side by side. Even when this was done there was some slight uncertainty as to the temperatures of Nos. 1 and 2, on occasions when the temperature of the air differed by 1° or so from that of the bath; for then the temperature given by a thermometer placed in the test tubes with the cells, differed somewhat from that of the water. In these cases the temperature of the thermometer in the tube was taken as the temperature of the cell. The other cells could not be immersed, and their temperatures were taken by a thermometer supported close to them. As in all cases, with one exception noted below, in which experiments were made, the air temperature varied very slowly, the uncertainty introduced was not large. In the numbers given in the Table, allowance has been made for the difference in temperature, if any, between the cells and the standard. The numbers are reduced on the assumption that the standard has the same temperature as the cell, and that its E.M.F decreases by 4·3 of our units per 1° C., and give the excess of the E.M.F. of the cell in question over our Standard No. 1 in all cases except those in which there is a special note.

It will be seen from the Table that the Cells 1, 2, 90, and 97, remained very close together throughout, and that too, over a considerable range of temperature. An exception must be made for No. 97 on November 3, when it was unaccountably low. Finding it remain so, we removed the zinc by withdrawing the glass stopper, and rubbed it on a clean silk handkerchief. We also dried and rubbed with emery cloth the upper part of the cell and the ebonite terminals to which the wires were attached. After this the cell recovered its value.

The experiments on November 19 were made with the object of testing the effect of a rather sudden change of temperature. The heating apparatus in the room had been turned off for about a week previous to November 18. After the observations of that day it was turned on, and the temperature of the bath rose about 5° C. in 24 hours. It will be seen that the cells are all wrong. The large cells 90 and 97 are too high (assuming the standard right). They have the E.M.F. corresponding to a lower temperature, lower by about 2°·5 C. The liquid which was saturated at 8°·5 has not had time to reach the state of saturation corresponding to the new condition. But the standard is itself too high, for No. 2 has fallen with respect to it by some seven divisions.

Now No. 2 is a smaller cell than No. 1 and contains more liquid. The zinc sulphate in No. 1 is very full of crystals, and it is reasonable to suppose that it takes

TABLE II.

Date	August, 1890.	February, 1891.	May 21, 1891.	July 20, 1891.	August 6, 1891.	August 10, 1891.	August 22, 1891.	November 1, 1891.	November 3, 1891.	November 14, 1891.	November 18, 1891.	November 19, 1891.	November 23, 1891.	November 30, 1891.	December 2, 1891.	December 7, 1891.	December 16, 1891.	December 22, 1891.	March 9, 1892.	January 11, 1892.
Temperature of No. 1 .	15	..	15·2	18	16·5	16·4	16·4	11·1	14·2	9·2	8·5	13·8	14·1	13·3	14·7	16	15·6	0	11·5	8·2
,, of other cells	..	..	15·2	18	16·4	16·4	16·4	11·1	14·2	9·2	8·5	13·8	13·1	12·9	14·5	15·5	15·4	0		
Cell No 2	..	..	0	..	−2	−2	..	..	−3	−2	−2	− 9	0	−1	−2	0	−1	−2		
,, 90	..	..	..	5	2	1	0	4	1	2	3	14	1	0	2	0	0	0		
,, 97	..	..	..	4	1	1	−1	−2	−7	−1	0	11	1	1	3	2	1	—	..	*—1
Temperature of cells .	15	16	15·2	..	17·6	17·4	..	..	..	11·1	..	..	..	..	..	..	16·2			
Cell No. 3A	..	..	−3	..	−3	..	..	..	..	− 8										
,, 3	−2	..	−6	..	−3	..	..	..	..	−20										
,, 4	−4	..	−5	..	−7	..	..	..	..	− 9										
,, 5	−5	..	−5	..	−6	..	..	..	..	− 7										
,, 6	−2	−1	..	..	1	3	..	..	..	3	..	..	..	..	..	..	3	..	*—	
,, 7	−2	−3	..	..	1	3	..	..	..	5	..	..	..	..	..	..	0	..	2	
,, 8	−1	0	..	..	2	4	..	..	..	5	..	..	..	..	..	..	3	..	3	
,, 9	0	0	..	..	1	4	..	..	..	5	..	..	..	..	..	..	3	..	4	
,, 10	0	0	..	..	1	3	..	..	..	3	..	..	..	..	..	..	2	..	3	

* Comparison with the Board of Trade Standard.

this semi-solid mass longer to reach the equilibrium condition than is required for the liquid in No 2.

To obtain the observations on December 22, the heating apparatus had been turned off and the windows of the room left open on the two previous nights. On December 21 there was a thick coating of ice on the bath which continued for one or two days; longer observations were made on December 22. Dr. SCHUSTER'S cell, No. 97, had been taken to London a few days previously.

A number of observations on the difference between the Cell No. 90 and the standard were made during the absolute determination of the E.M.F. Several of these confirm the fact that No. 90 gained its temperature equilibrium more slowly than No. 1. Thus, between the morning and evening of August 14, the temperature of the bath rose by 1°. The difference between No. 90 and No. 1 increased from 2 to 5 units.

Other observations again showed that it takes some time for No. 1 to change its value. Thus, on August 15, the bath was at 18°·1, and the air in the test tube round No. 1 was about 0°·5 higher; the difference in E.M.F. between Nos. 90 and 1 was 5. No. 1 was then taken out of the test tube and placed in the bath with No. 90. In about three hours the difference had fallen to 3, at which it remained for some time.

Similar effects were noted again during the early part of this year. On January 19 the room had been cooled down to about 9° C. About a week later the difference between No. 90 and No. 1 was 11, the temperature being 13°. The next day the difference was 8, and it was noticed that there was a thick compact layer of crystals at the bottom of the clear liquid. The cell was slightly shaken so as to mix up the sulphate of zinc which was clearly saturated below, but not above. The next day, Tuesday, January 26, the cells were together. On January 28, the temperature having risen to 15°, the difference had increased to 4; this increased to 5 the next day, the temperature of both cells being 16°, and some time more elapsed before the cells again came together.

It will be seen that the other cells are fairly near the standard.

Mr. ELDER'S H cells, 3*a*–5, are slightly too low, and it would appear as if their temperature coefficients were different.

The observation for No. 3, on November 14, shows distinct change, but we cannot attach great weight to the one isolated observation. It must be remembered, also, that it is difficult to read the temperature with great exactness.

It would appear as if Mr. CALLENDAR'S cells, Nos. 6–10, had risen in value between February and August. This is quite possible, for the insulation was originally somewhat defective—the wires from both poles of each cell were fastened down to a piece of deal.

It is probable, however, that their temperature, specially on November 14, is not very accurately known. The temperature of the room on that day, as indicated by a thermometer placed near the cells, rose by about 0°·4 in about an hour previous to the experiment, it is probable, therefore, that the E.M.F. of the cells corresponds to a temperature some few tenths lower than that given, and that the numbers are slightly too high; in any case the differences are small.

§ 15. *Tests on Old Cells in the Cavendish Laboratory.*

The cells of this set have been made at various dates by members of the advanced class in practical electricity at the Cavendish Laboratory, and are all of the pattern described by Lord RAYLEIGH ('Phil. Trans.,' 1885). Their comparison was begun in November, 1889, and has been continued. The standard against which the earlier comparisons up to December, 1889, were made is slightly doubtful, and also the temperature at which these were made.

The cells are interesting, for they show the kind of accuracy reached by experimenters putting up one or two cells from printed directions, with only such help as is usually given by the demonstrator. The materials have been purchased from the same sources as they were at the time when Lord RAYLEIGH was at Cambridge, and so they may be taken to be of approximately the same quality. Several cells belonging to this set have unfortunately been broken. Cell No. 23, which shows a very high E.M.F., is known to have been unsaturated with $ZnSO_4$.

TABLE III.

Date.	Nov. 7, 1889.	Nov. 13, 1889.	Dec. 3, 1889.	Mar. 16, 1891.	Mar. 21, 1891.	April 21, 1891.	May 2, 1891.	May 21, 1891.	Aug. 11, 1891.
Temperature.	..	..	..	13°	10°	13°	16°·4	15°·2	17°·6
Number									
11	+ 4	+ 0	..	− 4	+ 1	− 3	−3	−5	−1
12	+ 2	+ 8	..	− 5	− 0·5	− 5	−4	−6	−4
13	+ 8	+ 8	..	− 1	− 1	− 2	−3	−5	−1
14	− 4	+ 2	..	− 9·5	+ 4	−11	−4	−5	+2
16	+ 8	+16	..	− 0·5	− 2	+ 1·5	+7	−3	+3
17	+64	+16	..	− 5	−10	− 5·5	+2	−3	+6
19	..	..	+ 6	+ 0	− 6	− 1			
20	..	..	..	+ 0	+ 1	− 2·5			
21	− 4	+ 6	+ 0	− 2	− 7	− 5			
22	..	..	− 2	+ 0	+ 2	− 3			
23	+32	+36	+28	+31					
24	..	+ 8	+ 2	+ 2	+ 0	+ 1			

In these cells the paste was neutralised with zinc carbonate.

We come now to the observations on cells set up for the purposes of this enquiry.

§ 16. *Treatment of the Mercurous Sulphate.*

In studying the effect of variations in the materials, the impurities usually found in the mercurous sulphate appeared to be of primary importance. It is not easy to purchase this substance in a state of purity. The common preparations usually met with are either grey or very white. The grey powder contains mercury in excess; this does not appear to be hurtful to the cell; the white contains a considerable quantity of mercuric sulphate. This is shown by the substance turning yellow on adding water, with the formation of turpeth mineral or basic mercuric sulphate. This also is not harmful in small quantities, but its presence shews that the original powder has contained mercuric sulphate. This has been resolved by the water with the formation of the yellow substance and a soluble acid mercuric sulphate, and unless this process is complete and all traces of the original mercuric salt have been removed, error will be introduced.* Thus good cells may be set up with paste which is yellow at starting, provided the change is complete, but if the paste of a cell turns yellow after the cell has been made, it means that the mercuric salt is present, and this affects the E.M.F. On treating a sample containing mercuric sulphate with mercury, the mercuric sulphate is converted into mercurous, and may be used with safety.

The fact that the mercury mixes shows, as Mr. Swinburne has remarked, that the sulphate is bad, but the result of the mixing is that the evil is cured. This, then, is the *rationale* of the method of preparing the paste given in the memorandum. The washing with water resolves most, if not all, of the mercuric salt present into the yellow basic sulphate $3HgO.SO_3$, and the soluble sulphate $HgSO_4.2SO_3$; the latter is dissolved and removed. The shaking with mercury at a temperature near 30° removes any further traces of the acid mercuric salt. The temperature should not exceed 30°, for, when cooling from a temperature in excess of this, crystals may form which are not of the proper composition $ZnSO_4.7H_2O$.

§ 17. *Cells set up by Mr.* L. R. Wilberforce, *March*, 1891.

This set of cells was made by Mr. L. R. Wilberforce during March, 1891 (probably on March 19), and are in short test tubes with platinum wires fused through their bases for terminals. They cannot, therefore, be directly immersed in water. They were constructed with a view of finding the alterations in E.M.F. which would result from slight modifications in the materials and in the modes of preparing the cells. The last tests show them to be all in very close agreement amongst themselves and with cell No. 1.

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* According to Watts' 'Dictionary' the mercuric sulphate in presence of water becomes

$$\left\langle \begin{array}{l} HgSO_4.2SO_3 \text{ soluble.} \\ 3HgO.SO_3 \text{ turpeth mineral.} \end{array} \right.$$

We shall now describe the materials of which these cells were prepared.

The zinc rods in all were of pure stick zinc from Messrs. Johnson and Matthey. They were cleaned with a file and sand-paper, and generally washed in a little dilute sulphuric acid. They were allowed to stand in distilled water until required for use, when they were carefully dried.

The nature of each of the materials used in setting up the cells is indicated by Greek letters α . . . κ in the earlier columns of the Table (p. 596).

α is a saturated solution of zinc sulphate prepared by boiling a strong solution with zinc oxide, filtering whilst hot to remove excess of zinc oxide, and again when cold to remove the basic zinc sulphate $ZnO.ZnSO_4$, which had then crystallised. Afterwards it was evaporated to such a strength that crystals of $ZnSO_4.7H_2O$ separated at the temperature of the room. The solution was so thoroughly neutralised that it only turned a blue litmus paper to a port-wine colour. Although great care had been thus taken to remove all basic zinc sulphate, it is very probable that the solution still contained some traces of this compound.

β is a saturated solution of zinc sulphate prepared entirely below 30° C. Zinc carbonate was added to remove any excess of acid. This solution, when cooled to the temperature of the room, deposited crystals which were, without doubt, $ZnSO_4.7H_2O$. It turned a blue litmus to a port-wine colour. The reason for limiting the heating to 30° only was to ensure that the crystals separated on cooling should contain the right number of molecules of water of crystallisation. Solutions which deposit crystals above this temperature may give hydrates containing less water. The zinc sulphate had been prepared according to the directions of the 'British Pharmacopœia,' and was marked (Brit. Pharm.).

For the mercurous sulphate five different specimens were tried.

γ and ϵ are two samples of paste prepared in the same way from a specimen of mercurous sulphate supplied by Messrs. Harrington, of Cork. This substance was not pure, it contained some mercuric and basic mercuric sulphates, which was clearly shown by its turning bright yellow on adding water. These pastes were prepared by mixing at the temperature of the room some of the mercurous sulphate, a little pure mercury, and sufficient of the saturated zinc sulphate β to make a cream. This was vigorously shaken at intervals for two days before use. In general appearance it was white, with minute grey globules, which were collected in a more dense layer in the lower part of the bottle.

δ and ζ. These pastes were prepared at the temperature of the room from very pure mercurous sulphate and the zinc sulphate solutions α and β. The mercurous sulphate was prepared at the laboratory by precipitating pure mercurous nitrate (which was obtained by allowing an excess of pure mercury to stand with nitric acid), with sodium or potassium sulphate, when mercurous sulphate falls down as a white crystalline powder, and the nitrate of the alkaline metal remains in solution. This white precipitate is collected on a filter paper and washed with cold distilled water until the washings no longer give any reaction for a nitrate. It is useless to test the wash water for sulphate as mercurous sulphate is slightly soluble in water. The moist precipitate, after proper washing, is dried in a current of air at about 17° C. Prepared in this way, the powder, which is dull white, will not become yellow when moistened with water, nor will the water give an acid reaction. There is no mercuric sulphate present. It will slowly become grey if, whilst moist, it be exposed to light. ζ is a paste containing mercurous sulphate prepared according to this method. In the preparation of the mercurous sulphate for δ, however, very dilute solutions were used so that no immediate precipitate of sulphate came down. After four or five days white crystals about $\frac{1}{2}$ to 1 millim. in diameter separated. This is the purest mercurous sulphate we have used.*

η. The sample of mercurous sulphate in these cells was prepared from mercuric sulphate by reducing it with an excess of pure mercury. The white mercuric salt is placed in a mortar, and some pure mercury added, with sufficient water to convert the whole into a paste ; it is then ground until the whole becomes grey. The end of the reaction is easily recognised by the appearance of the surface of the globules of mercury, for, during the time that chemical action is going on, their surfaces will appear tarnished. The sulphate prepared in this way is grey with excess of mercury.

The various samples of mercury are denoted by θ, ι, and κ.

θ. Pure mercury distilled under reduced pressure in the laboratory.

ι. Mercury which had been used for general purposes, and was only filtered before being used for the cells.

κ. Mercury distilled in a small glass retort at atmospheric pressure.

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* A very useful suggestion is made by Mr. SWINBURNE in his paper before the British Association, 1891, in which he recommends the use of zinc sulphate solution for the purpose of precipitating the mercurous sulphate, and washing with saturated zinc sulphate to remove zinc nitrate. The sulphate then does not require drying.

Table IV.

Date.	Zinc sulphate.	Mercurous sulphate.	Mercury.	March 21.	April 21.	May 2.	May 21.	August 7.	August 11.	November 14.	December 15.	
Temperature				10	13	17	15	16·8	17·8	10·8	16·5	
Number.												
25	α	γ	θ	− 2	1	2	1	−1	2	2	0	
26	α	γ	θ	− 3	4	8	5	0	4	4	2	
27	α	δ	θ	1	6	7	6	0	3	2	2	
28	α	δ	θ	0	5	10	3	0	4	3	6	
29	α	ϵ	θ	− 2	− 1	1	3	1	2	1	−1	No crystals added
30	α	ϵ	θ	− 8	1	5	0	−2	2	2	4	Much crystals added
31	β	ζ	ι	−40	−16	−12	4	−1	3	6	3	
32	β	ζ	ι	−51	−28	−19	−25	−1	4	6	3	
33	β	ζ	κ	− 3	1	3	2	1	5	4	2	
34	β	η	κ	− 9	2	3	0	−1	4	4	0	
35	β	η	κ	− 5	− 8	− 2	− 6	−2	3	4	2	

The results are of much interest. All the cells are now within about 1 in 1000 of the standard; for, as we have said, one of our units is ·00025 volt; thus six of these units is ·0015 volt, or rather over 1 in 1000. The first six cells have been, it will be seen, nearly right from the beginning; those with the good mercurous sulphate δ were, two days after being set up, extremely close to the standard, while 25 and 26, 29 and 30, in which the bad sulphates, γ and ϵ, were used after treatment with the mercury, were rather too low. Nos. 31 and 32 were originally far too low; this would appear to be due to impurity in the mercury, for the zinc and mercurous sulphates were good, while the mercury was only cleaned by filtering. Moreover No. 33, which only differs from No. 32 in having distilled mercury, is nearly right.

The mercury used in Nos. 33, 34, 35 was distilled at atmospheric pressure, and the somewhat low results given by these cells may be due to this; in the case of Nos. 34 and 35 it would appear more likely that they have a similar source to the low numbers found in Nos. 25, 26, 27, and 30. The differences of E.M.F. had, however, been considerably reduced, except in the case of No. 32, some two months after making the cells, while at the next observation, after an interval of three months more, the differences had practically vanished. In the first three comparisons the reference to the standard was somewhat indirect; the absolute values of the numbers given cannot be trusted to very high accuracy, and the temperature is a little uncertain. It appears as if the values of the E.M.F. of Nos. 31 and 32 are still rising.

This set then shows the tendency of Clark cells made with different materials to settle down to the same value in time.

§ 18. *Cells set up by S.S. in March and April,* 1891.

This set of cells are all in short test tubes of the RAYLEIGH pattern, and were set up by one of us (S.S.) in March and April, 1891. They contain materials which are indicated as above by Greek letters. Some of these are the same as were used by Mr. WILBERFORCE; particulars of the others are given. λ. This paste was prepared from HARRINGTON's specimen of mercurous sulphate, which was washed by decantation and on a filter paper until the washings were no longer acid. During this operation the paste became yellow from the conversion of the mercuric sulphate present into basic mercuric sulphate and sulphuric acid. The basic mercuric sulphate or turpeth mineral being insoluble, remained with the mercurous sulphate, whilst the acid passed away with the washings. After washing, pure mercury was mixed with the paste, and heated with it in a pan of boiling water, with the view of attacking any yet undecomposed mercuric sulphate. The paste was allowed to remain with the mercury for two or three days, and then it was dried at the room temperature. To prepare it for use in the cells it was rubbed with saturated zinc sulphate to the consistence of a cream. The paste, therefore, contained mercurous sulphate, zinc sulphate, mercury, and traces of basic mercuric sulphate. This was an attempt to prepare the paste in accordance with instructions given verbally to one of us (R.T.G.) by Dr. ALEXANDER MUIRHEAD, to whose great knowledge of the subject we are much indebted.

Different mercury was used in some of these cells. This (μ) was a sample treated with nitric acid for some days, then washed and afterwards distilled *in vacuo*.

It will be seen from Table V. that the cells all start by being too low, but that in from three to four weeks of the time they were set up, the first seven, those made in March, have attained a steady value not far from the standard. The observation of 52, on August 7, is abnormal. The first six cells were lent for some other experiments in August.

The cells 50 and 51, made of the same materials as 25 and 26, agree with them in being too low. At first, the cells in which the mercury κ was used, are a good deal too low. Nos. 48 and 49 are of the same material as 27 and 28.

The first two tests recorded on these cells, made immediately after the cells were set up, were very rough, being performed by joining the cell up in opposition with another Clark, and passing a current from the two through a galvanometer and 20,000 ohms. They were merely intended to see that there was no great error. They give us, however, some important information, for the E.M.F. sank rapidly between March 17 and March 21, but regained its normal value by April 12.

The observations, given in Table IV., on Mr. WILBERFORCE's cells, Nos. 25–35, were made two days after they were set up, and we do not possess for them in such

TABLE V.

Date.	Zinc sulphate.	Mercurous sulphate.	Mercury.	Date of construction.	March 17.	March 18.	March 21.	April 12.	April 21.	April 25.	April 28.	May 2.	May 21.	August 7.	August 11.	November 14.	November 18.	November 19.	December 15.
Tempera-ture.					..	..	10	..	13	..	16·5	16·5	16·6	16·8	16·6	11·1	11·3	15	17·2
Number																			
48	a	δ	θ	March 17	− 1	− 4	−15	0	2	..	3	5	..	6					
49	a	δ	θ	,,	− 2	− 7	−11	0	2	..	4	4	..	4					
50	a	γ	θ	,,	− 6	− 8	− 3	1	3	..	2	3	..	0					
51	a	γ	θ	,,	−18	−12	− 9	− 5	− 5	..	− 9	− 8	..	− 5					
52	a	ζ	κ	,, 18	..	− 5	−24	− 5	− 4	..	1	0	..	9 ?					
53	a	ζ	κ	,,	..	−10	− 4	− 4	− 2	..	4	3	..	1					
56	a	η	κ	,,	..	..	−16	− 7	− 5	..	− 2	− 3	..	− 5	− 2	2	3	* 16	2
57	a	η	μ	April 25	..	..	..	..	..	− 2	14	..	..	18	21	4	4	16	17
58	a	η	μ	,,	..	..	..	..	..	− 2	14	..	..	− 4	− 5	−15	−12	3	2
59	a	λ	μ	,, 26	..	..	..	..	..	..	− 1	3	− 2	−23	−16	−30	−36	− 5	−39
60	a	λ	μ	,,	..	..	..	..	..	..	− 1	2	− 4	− 3	0	1	3	15	− 3

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* These observations are introduced to show the uncertainty introduced when sudden changes of temperature occur.

full detail the same information as to the changes which occur immediately after setting up. These do not occur in the cells 50, 51, and 53, at least to so marked an extent, but the effect is shown in 52.

Now, Nos. 50 and 51 are made of the same materials but crystals of zinc sulphate were added to 50, and the zinc rod was pushed a good deal further down so as to be well immersed in the paste which settles above the mercury. This may produce an important difference.

Nos. 57 and 58 were made simultaneously on April 25. The liquid used was purposely not warmed at all, and had been standing for some time in the room. It was saturated at the temperature of the room. The two cells agree in having a smaller temperature coefficient than the standard, but they differ in E.M.F. There is probably some slight difference in the temperatures at which the two are saturated. The results are only of interest as emphasising the importance often insisted on by others of introducing crystals of zinc sulphate, and making sure that they are in excess at all the temperatures at which the cell will be used.

In cells 59 and 60 the treatment was the same, except that in 59 the zinc rod was washed as usual with dilute sulphuric acid, and in 60 this was omitted. No. 60 has agreed with the standard throughout, in No. 59 there was a sudden and unexplained drop in E.M.F. between May 21 and August 7. Of the above cells, Nos. 57 and 58 are not Clark cells as defined in the specification. The others, with the exception of No. 59, attained their normal value within a month of being set up, and have retained it since.

§ 19. *Cells of Modified Pattern set up by* L.R.W. *and* S.S. *in March*, 1891.

The next set of cells were put up in the form indicated in the Board of Trade specification, p. 601, though at some time previous to its issue. The test tubes used, however, were rather larger, being about 10 cm. high and 2 to 2·5 in diameter. The platinum wires making contact with the mercury are enclosed in glass tubes, and were heated to a red heat before being placed in the mercury, so that proper contact was ensured.

Nos. 36 to 41 were put up by Mr. WILBERFORCE on March 18. In the first three the platinum wire is sealed into the glass tube which encloses it, in the last three this has not been done. On April 21 Nos. 36, 37, 40, and 41 were much too low, and it was noticed that there was a thick grey deposit on the zincs, the zincs from these cells and from No. 38 were withdrawn and scraped, they were then replaced and again tested, the results are somewhat too high, but from that time on, with the exception of No. 41, they have been fairly consistent. Nos. 61, 62, 63 were cells of the same pattern, made on March 18, by one of us (S.S.), at the same time as No. 56 and of the same materials, while No. 64 was made in the same way as No. 60 on April 24.

TABLE VI.

Date.	Zinc sulphate.	Mercurous sulphate.	Mercury.	Date of construction.	March 20.	March 21.	April 12.	April 21.	April 21.	April 23.	April 28.	May 2.	May 21.	May 25	August 11.	August 12.	August 15.	November 14.	November 23.	November 26.	December 2.	December 7.
Temperature.					..	10	..	13	16	14	16·5	16·6	15·2	..	16·8	16·9	18	9·4	13·3	13·8	14·9	16
Number.																						
36	β	ζ	κ	March 18	−43	−51	..	−15	4	3	4	− 1	− 4	..	1	− 1	2	3	..	..	..	1
37	β	ζ	κ	,,	− 6	− 5	..	−15	5	5	8	7	Broken									
38	β	ζ	κ	,,	− 5	− 2	..	0	3	3	7	5	3	..	1	− 1	3	3	..	..	..	3
39	β	ϵ	κ	,,	− 8	− 6	..	− 3	− 2	− 1	0	0	1	..	− 1	0	− 1	0	..	..	..	− 3
40	β	ϵ	κ	,,	−43	−57	..	−12	5	0	2	1	− 4	..	0	0	0	1	..	..	..	1
41	β	ζ	κ	,,	−43	−53	..	−35	5	−13	− 6	− 5	−10	..	− 9	0	− 9	− 8	..	..	..	..
61	a	η	κ	March 18	−12	−25	−13	−15	..	−14	− 8	−11	−18	−19	* ..	..	..	−16	− 2	− 2	1	3
62	a	η	κ	,,	− 6	−10	− 1	0	..	− 2	2	1	0	− 1	..	..	..	−17	−10	−10	− 9	− 3
63	a	η	κ	,,	−11	−33	− 7	−10	..	− 8	− 3	− 5	−14	−11	..	Broken						
64	a	λ	μ	April 26..	..	..	..	..	..	..	− 1	2	1	1	..	..	..	− 5	2	0	0	2

* The cells were used in the laboratory on one occasion early in June when 63 was broken. It is possible that 61 and 62 were interchanged then. The record after November 14 must be treated as a fresh one

The Table shows that while Nos. 62 and 64 are about right, Nos. 61 and 63 were decidedly too low, though at the time of the latest tests they are all fairly close together. Rough tests of the cells had been made on March 20, one or two days after they were set up. It will be seen that they were then too low, but that they afterwards got worse.

It thus appears that many of the cells we have examined up to this date began by being low, and that this fault increases at first; a grey deposit is also formed on the zinc. After a time, however, in most cases a change takes place, and in about a month or so the cells have ordinarily come right. In the case of this last set the natural development was stopped, and the fault corrected by scraping the zincs and removing the deposit.

It should also be noticed that the solutions are very free from acid.

§ 20. *First Form of Board of Trade Specification and Cells Set up in accordance with it.*

Early in May a provisional memorandum on the cell was prepared, and on May 25 six cells, Nos. 65 to 70, were set up by one of us (S.S.) in accordance with it.

Hopkin and Williams' mercurous sulphate was used and treated as prescribed in the memorandum annexed.

Memorandum on the Preparation of the Clark's Standard Cell.

Definition of the Cell.

The cell consists of zinc and mercury in a saturated solution of zinc sulphate and mercurous sulphate in water, prepared with mercurous sulphate in excess, and is conveniently contained in a cylindrical glass vessel.

Preparation of the Materials.

1. *The Mercury.*—To secure purity it should first be treated with acid in the usual manner, and subsequently distilled *in vacuo.*

2. *The Zinc.*—Take a portion of a rod of pure zinc, solder to one end a piece of copper wire, clean the whole with glass paper, carefully removing any loose pieces of the zinc. Just before making up the cell dip the zinc into dilute sulphuric acid, wash with distilled water, and dry with a clean cloth or filter paper.

3. *The Zinc Sulphate Solution.*—Prepare a zinc sulphate solution of pure ("pure re-crystallised") zinc sulphate by mixing in a flask distilled water with about twice its weight of crystals of pure zinc sulphate, and adding a little zinc carbonate to neutralise any free acid. The whole of the crystals should be dissolved with the aid of gentle heat; and the solution filtered, while still warm, into a stock bottle. Crystals will form as it cools, and when the solution is to be used a little should be taken from the bottom of the bottle near the crystals with a pipette. While this is being done the liquid should be at a decidedly higher temperature than that at which the cells will ordinarily be used.

4. *The Mercurous Sulphate.*—Take mercurous sulphate, purchased as pure, and wash it with distilled water. Drain off as much of the water as possible. Mix the washed mercurous sulphate in a mortar with the zinc sulphate solution, adding sufficient crystals of zinc sulphate from the stock bottle and a small quantity of pure mercury. Mix these well together to form a paste of the consistence of cream,

and then heat the paste sufficiently to dissolve the crystals, afterwards allowing the mixture to cool, and thus to form a saturated solution of mercurous sulphate in a saturated solution of zinc sulphate. The presence of the free mercury throughout the paste preserves the basicity of the salt, and is of the utmost importance.

Contact is made with the mercury by means of a platinum wire about No. 22 gauge. This is protected from contact with the other materials of the cell by being sealed into a glass tube. The ends of the wire project from the end of the tube; to one end a piece of copper wire is soldered, the other end and a portion of the glass tube dip into the mercury.

When tested it was found that the E.M.F. of all the cells was about 1 per cent. too high, though they agreed fairly among themselves. The cells were not saturated with the zinc sulphate, and were probably acid as well.

On May 26, Nos. 65 and 69 were opened, and crystals of zinc sulphate were inserted, while two days later 66 and 70 were also opened. Crystals were dropped into these latter cells and stirred into the paste.

The history of the four cells thus treated is given in Table VII. On August 14 Nos. 65, 69, and 70, with some other cells, were lent to Mr. E. H. GRIFFITHS. The history of these cells is continued in Table IX. Nos. 66, 67, and 68 have been tested from time to time since, with the result that No. 66 is about right, while Nos. 67 and 68 are not far apart, but are about 30 too high.

TABLE VII.

Date.	May 25.	May 26.	May 26.	May 27.	May 28.	May 28.	May 29.	May 30.	August 6.	August 10.	August 12.	August 14.	December 7.
Temperature . .	..	..	..	..	14·5	..	..	15	16·2	16·3	17·3	17·5	15
Number													
65	67	*	30	33	19	..	17	12	− 3	− 2	− 2	0	..
66	67	..	..	73	66	†16	14	21	10	8	7	9	− 4
67	67	..	..	71	65	..	60	59	60	61	..	..	30
68	62	..	..	69	61	..	56	61	58	60	..	..	30
69	72	*	15	26	10	..	8	5	− 2	− 2	− 2	0	..
70	68	..	..	68	59	†24	18	19	5	3	2	4	..

It will be noticed that these unsaturated cells were fairly close together from the first, and show every sign of continuing to give results which, though wrong, are consistent among themselves.

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* Crystals of zinc sulphate were inserted.

† Crystals of zinc sulphate were inserted and stirred into the paste.

§ 21. *Cells set up in accordance with the Second Form of the Specification.*

Of the cells described in Table VIII., Nos. 71, 72, 73 were made on May 30. The paste was prepared according to Lord Rayleigh's instructions, already quoted, from mercurous sulphate, supplied by Hopkin and Williams. The zinc rod was supplied by Harringtons, and is stated to contain a trace of iron. Before using the paste was shaken up with mercury. The mercury used in 72 and 73 was supplied by Hopkin and Williams as "pure redistilled."

No. 71 is Muirhead's portable form; the platinum wire is bent into a spiral, and dipped while red-hot into mercury. There is no free mercury at the bottom of the test tube.

Nos. 74, 75, 76 were made on June 3, and Nos. 77, 78, 79 on June 11, following the directions of the second form of the Board of Trade memorandum, which was issued June 23 (see p. 584). Mercury distilled in the laboratory was used; the zincs were from Harringtons, and the mercurous sulphate from Hopkin and Williams. The zinc sulphate, marked "Brit. Pharm.," from Hopkin and Williams, was used in all the cells. The cells Nos. 71–76 were taken to the Board of Trade towards the end of June, and brought back to Cambridge on July 18. Nos. 77, 78, 79 were lent to Mr. Griffiths on August 14. Details of their further history are given in Table IX.

It will be seen that the above cells, with the exception of No. 76, agreed with the standard to within one in a thousand from the beginning.

No. 73 was somewhat low during three tests in June, resembling in this respect the cells already put up; in all the other cases the agreement is very close.

Two comparisons with the Board of Trade standards are given at the end of the Table. These will be discussed later. The cells were brought back to Cambridge on July 20. Two other cells, Nos. 86, 87, were made on July 20 in the same way, using mercurous sulphate from Schuckharts. They were both within one of the standard.

Table IX. gives the tests on the cells lent to Mr. Griffiths. He made careful daily comparisons, using No. 43 as a standard. The results of two of his observations are given in the first two columns; the others were quite consistent. Nos. 69 and 70 were also treated by him as standards. The other four, Nos. 65, 77, 78, 79, were allowed to produce current through a resistance of 20,000 ohms.

On September 13 the E.M.F. of No. 43 fell suddenly by nearly two per cent., and gradually recovered, regaining its normal value on September 17. On September 18 No. 70 was too high, and continued so till September 23, when the tests ceased. On September 21 and 23 No. 43 was too low.

TABLE VIII.

																	Compared at the Board of Trade.	
Date . . .	May 30.	June 2.	June 3.	June 4.	June 6.	June 9.	June 11.	July 20.	August 6.	August 10.	August 12.	August 14.	August 22.	November 2.	November 14.	December 7.	July 7.	July 18.
Temperature . .	..	..	16	16	16	14·5	14·5	18	16·2	16·4	17·4	17·5	16·4	14·4	9·2	15	15	15
Number.																		
71	− 5	− 4	..	− 4	− 1	− 1	..	0	0	0	..	0	0	− 1	− 2	− 2	2	− 4
72	− 5	− 4	..	− 3	− 1	− 1	..	1	1	0	..	0	0	1	1	1	3	2
73	− 4	− 4	..	− 8	− 8	− 8	..	1	1	0	..	1	0	1	1	0	1	2
74	..	..	− 3	− 2	1	2	..	2	1	0	.	0	0	1	1	− 1	4	2
75	..	..	− 6	− 5	− 1	0	..	0	1	0	..	1	− 1	1	1	− 1	4	2
76	..	..	− 10	− 3	2	1	..	0	− 1	0	..	− 2	− 1	1	0	0	2	3
77	..	..	..	..	..	..	− 2	..	− 5	− 2	− 1	1						
78	..	..	..	..	..	..	− 2	..	0	− 2	− 1	1						
79	..	..	..	..	..	..	− 4	..	0	− 2	− 1	1						

Date . .		July 20.	July 21.	January, 1892.
Temperature.		18	16·2	17·4
Number.				
86	Made July 20, from SCHUCKART's sulphate	− 1	0	− 2
87		− 1	0	− 3

TABLE IX.

Date.	Sept. 12.	Sept. 17.	Nov. 11.	Nov. 23.	Nov. 25.	Dec. 2.	Dec. 7.
Temperature.	14·6	14·4	11·1	13·2	12·8	14·4	15·5
65	0	0	0	−4	0	0	−2
69	1	1	−6	−2	−1	−1	−3
70	−3	−3	−2	−3	−2	0	−1
77	−1	−4	3	−2	1	−1	−1
78	−1	−1	0	−5	−3	−1	−3
79	−1	−1	−1	−4	−2	−1	−3
43	S	S	1	−1	1	1	0

The cells were returned at the beginning of November. The tests given in Table IX. show that they have retained their E.M.F. with practically no change. Thus we may say that all the cells set up by us after the last date of the Board of Trade circular agree among themselves and with our standard to about one part in three thousand.

§ 22. *Errors Arising at the Zinc Pole. Effect of Amalgamation of the Zinc.*

After a cell has been made, the paste, which, when poured into the test tube is fairly homogeneous, and of the consistency of cream, separates into two portions. The more solid part, the mercurous sulphate, settles to the bottom, resting on the mercury, and a clear liquid remains on the top. The zinc rods used varied somewhat in length; in some cells they were entirely in the clear liquid, in others they extended partly into the more solid portion below. Various observations had shown us that this might produce some difference in the behaviour of the cell.

The differences appear to arise from the fact that when the zinc rod touches the mercurous sulphate it becomes properly amalgamated. A small trace of iron in the zinc, or in the zinc sulphate solution, does not, then, produce any serious effect. If, however, the zinc is only in the clear liquid, the amalgamation does not always take place. The zinc, instead, frequently becomes covered with a grey deposit. This grey deposit consists in the main of mercury in very fine globules, and when it is formed all over the zinc the E.M.F. of the cell falls, and it becomes unsteady.

The experiments recorded in Table X. show the effects of this deposit and of the method of treating it.

The cells in question were six, Nos. 42–47, constructed towards the end of April by Mr. L. R. WILBERFORCE. The materials of the cells are indicated as above, by Greek letters. They are of the Board of Trade pattern, but rather larger, being put up in test tubes about 10 cm. high and 2·5 cm. in diameter. It will be seen from the Table that while on April 27 they were nearly right, on May 2 they had most of them fallen considerably, and by May 26 they were, on the average, some 35 units too low. It

TABLE X.

Date.	Zinc sulphate.	Mercurous sulphate.	Mercury.	April 27.	April 28.	May 2.	May 26.	July 22.	July 23.	July 24.	July 30.	August 6.	August 7.	August 12.	November 11.	December 7.
Temperature.				17	16·5	..	..	..	..	..	..	16·2	16·2	17·6	11·1	15·8
Number.																
42	β	ϵ	μ	0	− 2	− 33	− 43	..	..	− 37†	− 30	− 11	− 10	− 4	− 5	− 1
43	β	ϵ	μ	− 2	− 30	− 40	− 43	− 34*	0	0	0	0	3	..	‡	..
44	β	ϵ	μ	− 1	− 4	− 34	− 42	..	..	− 32	..	− 30	− 32	− 21	− 3	1
45	β	λ	μ	3	− 1	− 8	− 31	..	..	− 21	..	− 29	− 26	− 23	1	2
46	β	λ	μ	3	− 8	− 27	− 32	..	..	− 23	..	− 31	− 26	− 23	− 17	0
47	β	λ	μ	− 1	− 31	− 38	− 35	− 32	..	− 34	..	− 43	− 36	− 35	0	4

* Amalgamated rod introduced, fell to − 8 at once.

† Fresh zinc inserted (? amalgamated).

‡ Amalgamated rods inserted in August, cells left unsealed till November.

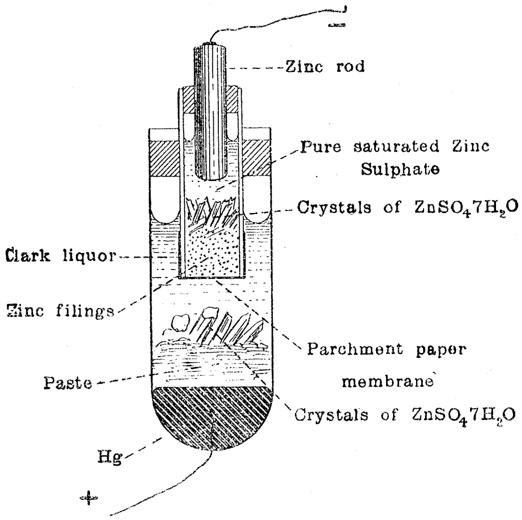
will be remembered that a good many other cells showed a fall at first, but most of them recovered in time.

The observations on July 22 show a tendency to recover here also.

The mercury used in the cells was the purest attainable, and the cells contained visible crystals of $ZnSO_4.7H_2O$ of the proper form. It was not possible, therefore, to attribute the fall of E.M.F. to impurity of the mercury or to supersaturation, and some other source had to be sought for the difficulty.

It was noticed that the grey deposit had formed on the zincs, and we had seen (see Table VI., April 20) that by removing this deposit a rise in the E.M.F. was produced. From this, and from some experiments which were being made on two cells, Nos. 80 and 81, it appeared probable that the fault lay at the zinc pole; that, in order that the cell should have its proper E.M.F., some action between the zinc and the soluble mercurial compounds was necessary, and that this action did not occur when the grey deposit was formed all over the zinc, but only when part, at least, of the zinc surface became bright. It is not clear whether the necessity for this action arises from impurities or from some other unexplained cause.

Fig. 4.



The diagram (fig. 4) shows how Nos. 80 and 81 were constructed. There is inside the cell surrounding the zinc rod a small glass tube, closed at its lower end by a membrane of parchment paper. On this is a layer of zinc filings. The tube surrounding the zinc is filled with saturated solution of zinc sulphate with an excess of crystals, and dips into the ordinary Clark liquor in the outer cell. Thus none of the soluble mercurial compounds in the liquor can reach the zinc pole, for in diffusing into the inner cell they have to pass the zinc filings which would react with them.

The cell is not really a Clark cell for the liquid in the glass tube is not a saturated solution of zinc sulphate *and mercurous sulphate.*

Observations on these cells showed that they were always considerably lower than the standard. After they had been compared the zinc of No. 80 was removed and amalgamated; the cell then became correct. This is shown in Table XI.

TABLE XI.

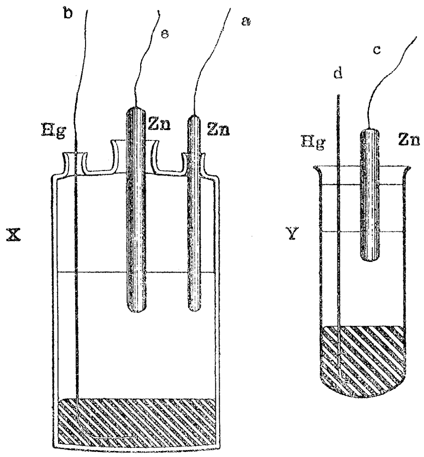
Number.	July 8.	July 9.	July 10.	July 11.	July 20.		July 21.	July 22.	July 23.	July 30.
80	− 25	− 24	− 26	− 23	− 19	Zinc amalgamated	+ 2	+ 2	+ 2	+ 8
81	0	− 53	− 29	− 23	− 21		− 16	− 15	− 13	− 20

Since the result of amalgamation had been to bring No. 80 into agreement with the standard it was thought worth while to try the effect of amalgamating the zinc of one of the cells Nos. 42–47 now under consideration. On July 22 the zinc rod of No. 43 which, as has been remarked, was covered with the grey deposit, was removed and amalgamated. After careful washing and drying it was restored to the cell which, since that date, has agreed well with our standard (see Table X.).

On July 24 the zinc rod from No. 42 was removed and a new rod inserted in its place. There is some doubt as to whether this rod was amalgamated or not; the entry in the note book is not quite clear; the cell was still too low, although better than before. The rod which had been taken out was placed in some fresh Clark liquor, and the difference of potential between it and a well amalgamated rod measured. It proved to be 8 or 9 units lower than the amalgamated rod.

Experiments were commenced on August 17 to test this point with a special form of cell.

Fig. 5.



A Clark cell was set up in a three-necked Woulfe's bottle. Two of the apertures, *a* and *b*, contained the ordinary zinc and platinum of the cell. The third, *e*, was left free for the insertion of the zincs to be tested. In fig. 5, X represents this cell and Y the Clark cell, the contents of which are to be examined, *d* being the platinum and *c* the zinc pole of Y. The plan of the experiment was to insert a well-amalgamated zinc in *e*, and compare the E.M.F. between *a* and *b*, *e* and *b*, respectively. These were practically the same, and equal to the standard Clark. The differences between their values and those of the standard are given in the first two columns of Table XII. In column 5 is given $c-d$, the difference between the E.M.F. of the Clark Y and the standard; it is negative, as Y had too small an E M.F. The zinc, c, was then transferred to the Woulfe's bottle, e being placed in Y. If the error is due to the zinc, and it retains its properties in the new liquid, the E.M.F. between b and c will be less than that of the standard, that between d and e will have its normal value, and there will be a difference of potential between the two zincs, a and c. On making the transference these effects took place, as is shown by the last three columns of Table XII., but the zinc c, when transplanted into the new liquor, rapidly changed, and the E.M.F. between b and c soon became nearly normal in amount. Columns 6 and 7 give the differences between the electromotive forces of $c-b$ and $e-d$, respectively, and the Clark; while column 8 gives the difference of potential actually observed between a and c. It is clear that some effect had taken place in the cell Y on the zinc which produced the low E.M.F. observed. The liquid of X acted in a short time on this zinc in such a way as to counteract this effect.

TABLE XII.

Cell.	Temperature.	Before changing zincs.			After changing zincs.		
		$a-b$.	$e-b$.	$c-d$.	$c-b$.	$e-d$.	Difference between a and c.
No. 47, on Aug. 19	17·2°	−1	0	−33	−11	−14	9
					− 9	− 4	8
						− 3	
						− 3	
						− 2	
					− 8	− 2	8
No. 46, on Aug. 19	17·6	−1	0	−23	−15	− 1	23
							10
							6
					− 6	− 2	6
No. 45, on Aug. 21	16·9	0	0	−23	−21		
					−20		
					−16		
					−15		
					− 8	− 3	
No. 44, on Aug. 21	16·8	0	0	−36	−50 } Immediately		
					−45 } after insertion		
					−35 } In a few		
					−30 } minutes		
					−25		
					−18		
					−10	− 1	
					− 7		

Since with the new zincs the cells Y give normal readings, we infer that the rest of their contents were not at fault, though there probably was some difference between the solutions in X and Y, for the zinc from Y soon became right when put into X.

Since the new zincs were inserted the cells have remained nearly normal.

It will be remembered that the fall noted in the cells described in Table VI. was also corrected by the removal of the grey deposit.

The evidence we have collected on these points is not conclusive, and we are still engaged in experiment. There is no doubt that there is a tendency in many cases for cells set up with good materials to fall in E.M.F. at first. This drop appears to reach a maximum, and in good cells to correct itself fairly soon. In other cells the recovery is very slow; indeed, the experiments must go on for some time longer before we can say in all cases whether it will be complete. In such cells a grey deposit is formed on the zinc. This deposit is mainly mercury.* On removing it from the zinc the E.M.F. rises; the same is the case on substituting an amalgamated zinc for the original one; but it is not clear whether this happens because some action of the nature of amalgamation is required to prevent slight impurities in the zinc sulphate from having an injurious effect, or because even with a pure zinc and mercurous sulphate solution an amalgamated surface is required, or again, because the action which has led to the formation of the grey deposit has removed from the solution injurious impurities. These points are still under examination.

We are also inclined to think that a trace of acidity in the solutions is useful in preventing the formation of the grey deposit; on this point also we are continuing the work.† The slight acidity in time corrects itself by its action on the zinc. The important fact remains that the formation of this grey deposit must be, as far as possible, prevented, and, if it does form, the deposit must be removed.

The experience of Dr. SCHUSTER with regard to this grey deposit somewhat resembles our own. He has kindly sent us the results of measurements of a set of rather large cells prepared from commercial sulphate.

Soon after being set up these cells were tested against some cells made two years since. Taking the E.M.F. of this set as unity, the new cells were as follows:—

---

* It is only necessary to dip the grey covered zinc rods for a moment in a dilute acid to obtain a bright amalgamated surface; no fresh mercury is required. Dr. SCHUSTER informs us in a letter that he has analysed the grey deposit, and found it to be nearly pure mercury.

† The solutions used in the bad cells Nos. 42–47 were, as tested by litmus paper, distinctly less acid than those employed in the good cells Nos. 72–79. While the solution in the cell No. 90 is now less acid than that in the bottle from which the cell was originally filled.

Date.	January 23.	January 30.	February 6.	March 11.
Number.				
5	·9777	·9587	·9633	1·0005
6	·9823	·9590	·9658	1·0072
7	·9848	·9627	·9629	1·0159
8	·9969	·9516	·9626	·9943
9	·9892	·9632	·9711	
10	..	·9695	·9459	

Writing in May, 1891, Dr. SCHUSTER says:—

"My present opinion is that the cell only arrives at its steady state after some action has taken place between the zinc and the solution, and it is necessary that the zinc surface exposed should not be too small compared with the quantity of liquid. At any rate, most of my large cells prepared with good sulphate seem to settle down at an E.M.F. about $\frac{1}{3}$ per cent. too low, and the lower the smaller the surface of zinc exposed. Amalgamation seems a mistake, for it is just the action of the zinc previous to amalgamation which brings the cell into a steady state."

Writing at a later date, February, 1892, Dr. SCHUSTER expresses the opinion that the action required to bring the cell to a steady state is the formation of a basic zinc sulphate. This process may be facilitated by the introduction of zinc oxide into the cell, and in that case amalgamation will probably be an advantage, but if the cell is left to settle down of itself, the process of amalgamation helps the formation of the basic zinc sulphate, and it is desirable, therefore, that this process should go on in the cell.

He also tells us that in the cells made in the Reichsanstalt at Berlin the zinc sulphate is boiled with zinc to secure the formation of the basic salt.

On this point, however, our own view would be somewhat different from that expressed by Dr. SCHUSTER, for it has been observed by one of us (S.S.), and by Mr. E. H. GRIFFITHS, and is in accordance with the chemical theory of the interchange of bases, that the mercurous sulphate which is used in preparing the paste reacts with the basic zinc sulphate, producing zinc sulphate and probably basic mercurous sulphate; thus, if the zinc oxide used to neutralize the zinc sulphate does form with it a basic salt, the mercurous sulphate clears this out of the solution.

Dr. SCHUSTER has also confirmed our results as to the danger of the grey deposit and the rise in E.M.F. produced by removing it.

Mr. SWINBURNE, in his paper already quoted, also recommends amalgamation. He found differences of potential amounting to ·4 per cent. of the E.M.F. of a Clark cell between different specimens of zinc immersed in saturated zinc sulphate. These he assigns partly to "impurities, probably iron, in the zinc sulphate." They disappeared, practically entirely, when the zincs were amalgamated.

It may be noted that Lord RAYLEIGH did not meet with this source of error, for his zincs, being generally plunged into the more solid part of the paste, were immediately amalgamated.

§ 23. *Effect of Shaking on the Cells.*

The history of these cells illustrates another point. Dr. HOPKINSON called our attention to the fact that he had observed that while slight mechanical shaking did not affect the E.M.F. of a good cell it produced considerable change in the E.M.F. of one which was too low. This fact we have repeatedly verified.

Thus, on August 12, Nos. 41, 45, 46, and 47 were all to low. Their E.M.F. in each case rose considerably when the cell was tapped, but fell back towards the old value when the tapping ceased. Cell No. 40 was right, and no effect was produced by tapping it.

The effect of the shaking would appear to take place through its bringing fresh zinc surfaces into contact with the solution.

A similar result took place with some cells which were too high, only, in this case, the E.M.F. was lowered. Thus, on August 6th, No. 68 was 56 too high; on tapping, its E.M.F. fell till it was only 23 too high; it then rose to about its original value; and hence, on further tapping, fell to within 5 of the standard. Cells No. 71 and 72 were quite unaffected by the tapping, remaining within 1 or 2 of the standard throughout. Another cell sent us to test was about 20 too high; on slight tapping it fell to about 10.

Thus, it appears that slight tapping produces a change in bad cells; we have never found it produce any change in good ones.

§ 24. *Mr.* E. H. GRIFFITHS' *H Cells.*

Table XIII. contains details of a set of H cells, constructed in February, 1888, by Mr. E. H. GRIFFITHS, which have been subject to much careful examination. They were tested against the Board of Trade cells. The results are important, because the cells are very consistent among themselves, and, at the same time, they are undoubtedly wrong. They appear to be unsaturated, and have, in consequence, a lower temperature coefficient than our cells, and agree with them more nearly at low than at high temperatures. It is clear, then, that a set of cells may be made which will agree among themselves, and yet be wrong. Mr. GRIFFITHS writes as follows of the materials used :—

"Re-distilled zinc and mercurous sulphate were used. The solution of zinc sulphate was allowed to stand and not used unless it deposited crystals of the proper form. The mercury was some which I had purified and distilled myself."

The first three series of observations given in the table were made by Mr. GRIFFITHS. The temperature was in each case nearly 15°, and the observations were corrected to 15° by the use of Lord RAYLEIGH'S coefficient. This coefficient is clearly wrong for these cells, as the observations show, but the error produced will be small. The change per 1° relative to our standard is about 2·8 of our units. Our standard changes by about 4·5 units, so that the change in the Griffiths cells is only about 4·5 — 2·8 or 1·7, and this implies a coefficient of about one-third that of the standard cell. The last column gives the values found at the Board of Trade in terms of their standards.

This, and the cells described in Table VII. are, so far as our experience has gone, the only sets of cells which have been quite wrong and yet have remained consistent among themselves for some time, and that over a considerable range of temperature.

TABLE XIII.

Date.	August, 1888.	December, 1888.	August, 1890.	August 8, 1891.	August 10, 1891.	November 14, 1891.	December 16, 1891.	March 9, 1891.*
Temperature	15	15	15	16·8	17·4	11·1	16·2	11·5
Number.								
91	26	27	26	26	29	12	23	12
92	28	29	28	28	31	15	26	15
93	24	24	24	25	27	10	22	11
94	28	28	26	26	28	12	24	12
95	28	28	26	27	29	12	24	13
96	28	28	28	28	31	14	25	14

§ 25. *Comparison with the Board of Trade Standard Cells.*

A means of comparing the E.M.F. of our cells with those of the standards of the Board of Trade at Westminster, which were set up by Dr. MUIRHEAD, is afforded by the last columns of Tables II., VIII., and XIII., which give, in terms of the unit we have adopted, viz., ·00025 volt, the differences between our cells and the standards of the Board of Trade. The comparisons were kindly made for us by Mr. RENNIE, Major CARDEW's assistant. It will be seen at once that the agreement is very close. For the cells Nos. 7, 8, 9, 10, Table II., constructed by Mr. CALLENDAR, the differences observed are rather greater than those found by us either before the cells were sent or soon after they returned.

The last two columns of Table VIII. give the results for the five cells Nos. 71–76 No. 71 appears to have been low at one of these observations, for the rest we see that the differences are rather greater than those with our own cells.

---

* Comparison with the Board of Trade standards.

A similar comparison is also afforded by the last column on Table XIII., and here there is almost exact agreement between our results on November 14 and the Board of Trade measurements on March 9.

The standards would appear to be exactly equal, but these observations hardly deserve as much weight as the others, for the temperature of the large H cells is not very easy to be sure of.

It would seem then the Board of Trade standards are lower in E.M.F. than our standard by, possibly, one or two of our units, that is, by about ·0003 volt. This clearly is very small. The Board of Trade standards are a set of 72 cells constructed by Dr. MUIRHEAD. These cells are from time to time compared against each other, and Mr. RENNIE states that the greatest variation among them is less than ·00068 volt, that is, distinctly under three of our units. The cells used were known to be good average cells.

Dr. SCHUSTER'S cell No. 97 was taken to London on December 21, and on January 11 it was compared, with the following results given by Mr. RENNIE.

At 8°·0 C. the E.M.F. of B.T. 822/35 exceeds that of SCHUSTER'S cell by 0·00021 volt.

At 8°·1 C. the excess was 0·00017 volt.

At 8°·3 C. the E.M.F. of B.T. 822/34 was less than that of SCHUSTER'S cell by 0·00005 volt.

Thus SCHUSTER'S cell lies between the two Board of Trade standards, and falls short in E.M.F. of the mean of the two by less than one of our units.

§ 26. *The Temperature Coefficient of the Cells.*

We have also made some experiments with a view of investigating the temperature coefficient of our cells.

It has already appeared from Table II. extending over a range of temperature from 0° to 18° that our more important cells, including the standard Rayleigh 1, have practically the same coefficient. When we were engaged in the experiments in August we did not expect them to be continued so long, and therefore a cell was fitted up which could be packed in ice.

It was a cell of the ordinary form, but contained a delicate thermometer, the bulb of which was in the paste. The cell was placed inside a long test tube, packed with glass-wool and asbestos; the thermometer passed through a cork closing the test tube. The stem of the thermometer was so long that most of its graduations were outside the cork. It could be read, therefore, without seriously disturbing the cell when packed in ice. With this cell a number of measurements were taken.

The results of these are given in the accompanying Table XIV.

TABLE XIV.

Date.	Temperature of cell.	Difference from No. 1.	Temperature of No. 1.	Notes.
August 10	16°·4	0	16°·4	
,, 2.30	16·7	0	16·7	Packed in ice.
,, 3.50	..	51		
,, 4.30	..	63		
,, 5.30	..	71	16·7	Readings still changing.
August 12, 10.30	0	74	16·9	Repacked in ice at 10.32.
,, 10.55	0	74	16·9	
,, 1.15	0	74	17	
,, 4.30	0	75	17	Repacked at 5.10.
,, 5.15	0	75+	17·1	
,, 7. 0	0	76	17·4	
August 13, 10. 0 A.M.	0	74	16·7	Placed in water of temperature 16°·7 at 10.5.
,, 10.30	13	30		
,, 11. 5	16·6	11		
,, 6.10	17·5	6	16·7	
August 14, 9.40	17·8	7	17·7	
,, 4.50	18·8	7	18·5	
August 15, 10. 0	18·4	6	18·4	Placed in water at 32° at 12.30 on August 17, and allowed to cool.
August 18	18·3	2	18·3	
,, 19	17·2	2	17·2	
November 2	14·4	1+	14·4	Cells all at one temperature.
,, 14	9·2	1+	9·2	
December 22	0	2−	0	

When the cell was left on August 10 the readings were still changing though it had been in ice for three hours.

On August 11 it appeared that some moisture had got among the glass-wool, the cell was taken out and repacked, taking care to insulate the leads thoroughly with gutta percha. After this the difference rose to 66, but was still increasing at 5.40. Throughout the next day and up to 10 A.M. on August 13 it was steady, the mean reading being 74·6, and the average temperature of the standard 17°. After the last observation the cell was placed in water at 16°·7. At first there was a rapid fall, but after a time the fall ceased and a steady difference of some 6 or 7 of our units persisted all through the next day.

On August 17 the cell was placed in warm water at 32° and allowed to cool. On August 18 the difference at about 18° was 2, and this continued through the next day. Before the cell was placed in ice the difference between it and the standard was 0. The mean gives us as the difference when the two cells are at the same temperature the value 1, so that the change for 17° is 74·6 — 1, and the change per 1° C. is 4·33.

On August 12 the E.M.F. of the Clark was found to correspond to 5736 of our units, and we have then as the coefficient of change of E.M.F. with temperature the value 4·33/5736 or ·000755. Lord RAYLEIGH gives as the value of the coefficient from about 0° to about 15° ·000765, for another it is ·00073, and for a third ·00083.

The last three observations in Table XIV. show that for a range of temperature from 14°·4 to 0° our cell and Lord RAYLEIGH's cell No. 1 have the same E.M.F.

When the cell was put into the warm water on August 17 readings were taken of the E.M.F. and temperature.

About half-an-hour after being put into the bath the E.M.F. was 45 units below the standard, the temperature was 31°, that of the standard 17°·3. The readings remained steady at this for five minutes.

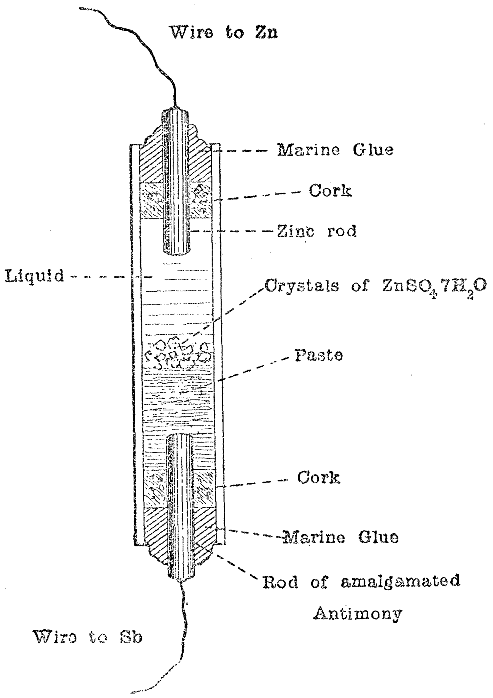
This would correspond to an increase of only about 3·3 units per 1° C. instead of 4·3, and again emphasizes the fact that the E.M.F. of the cell is not a fixed quantity at a given temperature unless the temperature has remained steady for some time previously.

Most of our cells were compared with the standard at various temperatures between 9° and 18°. The observations show that all the cells except those known to be unsaturated have the same coefficient, and the average value of that coefficient between 0° and 15° is ·00076. Our experiments do not show whether the relation between E.M.F. and temperature is linear or not.

§ 27. *Portable Form of Cells.*

Cells which contain much mercury are not suitable for carrying about for testing purposes, as the mercury may be thrown in contact with the zinc rod and become contaminated with zinc. It has been shown that a very small percentage of zinc dissolved in mercury causes that to behave as though it were zinc. To avoid the use of much mercury cells have been constructed with merely an amalgamated platinum wire for their negative metal. The platinum being more negative than mercury does not interfere with the E.M.F. of the cell. Cell No. 71, described in Section 20, is constructed with an amalgamated platinum wire. Since it is only necessary to use a metal more negative than mercury for the negative pole and to amalgamate its surface, we have tried the use of small antimony rods. A small rod of antimony is cast and boiled in mercury to amalgamate its surface. It is then fitted into the cell, as shown in the diagram, fig. 6. It is of importance that the antimony be pure, for should it contain metals more positive than mercury the electromotive force of the cell will be reduced by their solution in the mercury. For this purpose, therefore, antimony metal reduced from pure tartar emetic should be used.

Fig. 6.



With a large stout antimony plate cells of low resistance could easily be made. The tests made on this cell are shown in the following table.

TABLE XV.

No.	July 9.	July 10.	July 11.	July 20.	July 21.	July 22.	July 30.	Aug. 6.	Aug. 17.	Nov. 14.	Dec. 16.
			18°	18°	19°	18°·5	17°	16°·6	17°·2	11°·1	16°·2
82	−32	−5	−9	−3	−2	−3	−3	−5	−3	2	−2
83	..	..	..	..	−6	−4	−4	−5	−4	3	−3

Cell 82 was made on July 9th, 1891.
Cell 83 was made on July 21st, 1891.

During several of the tests the cells were inverted top to bottom without producing any effect. It is clear that at temperatures of 16° to 18° they are rather less than the standard, while at 11° they appear to be greater. Thus their temperature coefficient is rather greater than that of the usual form. Over the range worked with the difference between their E.M.F. and that of the standard is well within ·1 per cent.

§ 28. VON HELMHOLTZ *Standards.*

In the 'Sitzber. der Akad. der Wiss., Berlin,' 1882, p. 26, VON HELMHOLTZ has described an electromotive force standard consisting of mercury, mercurous chloride, zinc chloride, and zinc. Similar cells have been prepared and used by OSTWALD ('Zeitschrift für Physikalische Chemie,' vol. 1.) We have prepared a set of six cells like these, and have tested them at intervals. They are put up in small test tubes, with platinum wires sealed through the bases. The solution of zinc chloride was prepared from solid sticks of zinc chloride, and therefore probably contains some oxychloride. It had a specific gravity 1·445 at about 15°. Since the solution alters in strength if a current be taken from these cells, it is necessary to be very careful that they do not become short-circuited. These cells had an E.M.F. of about ·98 volt; if the solution be taken slightly more dilute they may be adjusted to be exactly 1 volt at 15°. OSTWALD has attempted to do this, and states that it is secured by using a solution of specific gravity 1·41.

Three series of observations were made of these cells, and the following table gives the results in terms of the E.M.F. of a Clark as unity at the temperatures mentioned.

TABLE XVI.

Date	February 17.	March 16.	August 22.
Temperature .	16	13	17·4
Number.			
101	6890	6879	6892
102	6891	6882	6894
103	6892	6882	6895
104	6890	6879	6892
105	6891	6882	6892
106	6891	6882	6894
Mean	6891	6881	6893
Value in volts .	·9876	·9881	·9870

The last line gives the value in volts, assuming the E.M.F. of a Clark at 15° C. to be 1·4242 volt.

The absolute values at the earlier dates are somewhat uncertain because of the uncertainty attaching to the actual value of the Clark used as standard. In this case the values, on February 17, were referred to CALLENDAR's cells, but it is clear that the cells cannot have changed much, and that they retain unaltered their relative values.

§ 29. Gouy's *Cells.*

Another modification of the cells has been suggested by M. Gouy ("Sur une Pile Etalon," 'Journal de Physique,' 1888.)

It consists of zinc, zinc sulphate, mercuric oxide, and mercury. According to M. Gouy, the E.M.F. at any temperature, t, is given in legal volts by

$$E = 1{\cdot}390 - {\cdot}0002\,(t - 12).$$

The zinc sulphate solution is prepared by boiling a saturated solution for an hour with a few thousandths of its own weight of oxide of silver. The liquid, when cooled and filtered, has sticks of zinc put into it, which precipitate any silver remaining. Four cells were made; of these two, viz., Nos. 54 and 55, contain the yellow oxide, the other two, Nos. 88 and 89, the red oxide of mercury. The values of the E.M.F. have been reduced to 12° by M. Gouy's coefficient.

Table XVII.

Numbers . . .	54	55	88	89
Values . . .	1·3794 1·3803 1·3806 1·3809	1·3793 1·3806 1·3869 ..	1·3906 1·3867 1·3890 1·3839	1·3896
Mean	1·3803	1·3823	1·4875	1·3896
Mean of two . .	1·3810		1·3879	

To reduce them to "legal volts," and so to compare them with M. Gouy's results, we must multiply these results by the ratio 1063/1060, we have thus the values 1·385 and 1·392. The latter is nearly 2 parts in 1000 above M. Gouy's result.

APPENDIX.

(August 18, 1892.)

§ 30. *Further Comparisons of the Cells already described.*

Since the foregoing paper was communicated, the experiments have been continued, and numerous other results have been obtained. The more important of these are described in the following Appendix. The cells already described have been repeatedly compared with the standard.

TABLE XVIII.

CELLS described in Table II.

	No. of cell.										
	2	90	3*a*	3	4	5	6	7	8	9	10
Difference, Dec., 1891 . .	−2	0	−3*	−3*	−7*	−6*	3	0	3	3	2
„ July, 1892 . .	−2	1	−1	−2	−4	−1	1	3	3	3	3

CELLS described in Table IV.

	No. of cell.										
	25	26	27	28	29	30	31	32	33	34	35
Difference, Dec., 1891 . .	0	2	2	6	−1	4	3	3	2	0	2
„ July, 1892 . .	3	broken	2	2	1	1	3	3	3	3	3

CELLS described in Tables V. and VI.

	No. of cell.														
	56	57	58	59	60	36	37	38	39	40	41	61	62	63	64
Difference, Dec., 1891. .	2	17	2	−39	−3	1	. .	3	−3	1	. .	3	−3	. .	2
„ July, 1892. .	0	17	6	−36	−6	. .	. .	1	−1	0	0	2	2	. .	−8

* These observations were made in August, 1891.

CELLS described in Tables VIII. and IX.

	No. of cell.											
	71	72	73	74	75	76	65	69	70	77	78	79
Difference, Dec., 1891 ..	−2	1	0	−1	−1	0	−2	−3	−1	−1	−3	−3
,, July 14, 1892..	−1	−1	−1	−1	−3	−5						
,, ,, 21, 1892..	−2	−1	−1	−1	−1	−2	0	−3	−1	−1	−1	−1
,, ,, 22, 1892..	−3	−1	−1	−1	−1	−2	1	−4	−1	−2	−2	−3

CELLS described in Tables X. and XV.

	No. of cell.							
	42	43	44	45	46	47	82	83
Difference, Dec., 1891..	−1	1	1	2	0	4	−2	− 3
,, July, 1892..	−9	−1	−4	−2	−1	−1	−2	−16

The results of comparisons made at the end of 1891, and of the latest comparisons we have made, are given in Table No. XVIII. The Table shows that, with few exceptions, the relative values of the cells remain closely the same as before.

It will be remembered that Nos. 57 and 58 were known to be unsaturated, while No. 59 dropped suddenly in value between May and August, 1891, and has remained low ever since.

The behaviour of No. 76 requires some notice. Some comparisons were made on July 13 and it was observed that it was then five units too low. This continued on July 14; but when the cells were next tested, on July 21, it had recovered, and has since remained right, having been frequently re-tested. The cause of this is not quite clear, but it is probable that it was due to the following circumstance:—The binding screw which connected No. 76 to the circuit was allowed by accident to fall into the bath; the water was dirty, having been standing for some time; and possibly some of the moisture adhered to the screw, and set up a small E.M.F. at the junction. It was found by experiment on July 21 that, by wetting this binding screw, small changes could be produced in the E.M.F. observed.

With this exception, the sets Nos. 71 to 76 and 65 to 79 show very steady agreement. These, it will be recollected, are cells set up in accordance with the second form of the Board of Trade Memorandum.

The set Nos. 42 to 47 shows some change. These are the cells from which the grey deposit was removed. They were left unsealed for some time, and after the treatment to which they have been subjected, can hardly be considered standards.

In June the portable cell No. 82 was sent by parcel post to London, and thence to Manchester, where it was compared by Dr. SCHUSTER with his standards. About the same time No. 83 was taken to Manchester by one of us (R. T. G.) in a handbag. The cells were brought back to Cambridge in a portmanteau which travelled as passenger's luggage. Dr. SCHUSTER found that No. 82 was less than his standard by two of our units, while No. 83 was less by six units. The Table shows that on their return No. 82 had not changed relative to our standard, while No. 83 had varied considerably. Other comparisons confirmed these results.

A large number of comparisons have been made from time to time between the large bottle cell, No. 90, and the standard. The two remain practically equal so long as the temperature remains steady for some time, but some experiments in March and April emphasize the importance of maintaining this very constant, at any rate, for large cells.

Towards the end of March the weather was very cold. On March 30 the room temperature was 6°; it had been lower, and the baths in the room were as low as 3°·5; the cells were not examined at this date. On March 31, when the bath was at 10°·8 C., No. 90 exceeded the standard by nine units. On April 1, the temperature being 11°·2, the difference was five units. A rod was then put through a hole in the cork of the bottle cell, and the zinc sulphate was stirred up. The difference fell immediately to less than one unit, the temperature remaining unchanged. Thus, on March 31, the E.M.F of No. 90 corresponded to a temperature more than 2° below the temperature of the cell, and on April 1 it was still too high by an amount equivalent to the change due to 1 degree. The crystals had formed in a hard mass on the top of the paste; the zinc was some little way above these, and the E.M.F remained too high until they were broken up.

§ 31. *Cells set up by Mr.* E. H. GRIFFITHS.

In January and February of the present year, Mr. E. H. GRIFFITHS set up a number of cells, following in the main the directions of the second issue of the Board of Trade Memorandum. These cells are numbered from 131 to 160. In one batch of these, No. 149 to 154, the zinc sulphate was treated with mercurous sulphate in the manner described on page 611.

We give the description of these cells, kindly furnished to us by Mr. GRIFFITHS, to whom our best thanks are due.

Cells Nos. 131–142, made January 26, 1892. Chemicals supplied by HARRINGTONS. The $ZnSO_4$ was saturated at 33° C. The Hg_2SO_4 was used as supplied, except that it was shaken up with mercury, but not washed.

Cells Nos. 143–148. January 31, 1892. The Board of Trade directions followed implicitly.

Cells Nos. 149–154. February 6, 1892. To the $ZnSO_4$ solution saturated at 33° C., neutralised with ZnO and filtered at 30° C., a small quantity of Hg_2SO_4 was added, and the black deposit was filtered off. In other respects the cells were the same as 143–148, the Board of Trade directions being followed. These cells assumed the standard E.M.F. immediately on formation.

Cells Nos. 155–157, made according to Lord RAYLEIGH's directions from paste which had been in stock since Michaelmas, 1889.

Cell No. 158 the same as Nos. 131–142, except that the zinc was amalgamated.

Cell No. 159 the same as Nos. 143–148, except that the zinc was amalgamated.

Cell No. 160 the same as Nos. 149–154, except that the zinc was amalgamated.

Cells Nos. 131–136 were compared with our standards repeatedly for about a fortnight after being set up, and showed very close agreement.

The other cells were compared by Mr. GRIFFITHS with our cell No. 65; the set of cells described in Table IX., viz., Nos. 65, 69, 70, 77, 78, 79 had again been lent to him for this purpose. It appears from our Tables that No. 65 is in very close agreement with our standard, and we may take, therefore, this comparison as giving the E.M.F. of Mr. GRIFFITHS' cells in terms of the standard.

TABLE XIX.—Cells constructed by Mr. E. H. GRIFFITHS.

	Date.	Number of cell.														
		131	132	133	134	135	136	137	138	139	140	141	142	158	143	144
Differences	Feb., 1892	1	1	1	1	2	2	0	1	1	1	2	2	3	2	1
,,	July, 1892	0	0	1	0	−1	0	1	1	1	1	0	0	−1	3	2
		145	146	147	148	159	149	150	151	152	153	154	160	155	156	157
Differences	Feb., 1892	1	1	2	0	−1	−1	−1	0	−1	0	−1	0	−4	−4	−4
,,	July, 1892	2	3	3	2	2	0	0	0	0	0	0	0	−4	−4	−4

Table XIX. shows the results; the unit is slightly less than in our measurements, being about ·0002 volt.

In February the temperature was about 13°, in July it was 14·4.

It will be seen that the cells are all fairly close to the standard. Nos. 131–148 are on the whole a little too high. A comparison between Nos. 158, 159, and 160, with the batches immediately preceding them, respectively shows that amalgamating the zinc has in these cases no distinct effect; the mercurous sulphate in the solution of itself insures amalgamation in the cell.

The series, Nos. 149–154, in which Mr. GRIFFITHS' method of clearing the zinc oxide or basic zinc sulphate from the solution by the action of mercurous sulphate and filtration was employed, is most closely in agreement with our standard, and this agreement was attained immediately after the cells were set up. It will be noticed, however, that the cells, Nos. 155–157, in which the old paste was used, are too low by about ·0008 volt, though they agree well together.

§ 32. *Professor* Ayrton's *Standards.*

By the kindness of Professor Ayrton we have been able to compare two cells set up Dr. Muirhead, and used as standards at the Central Institute, with ours. These two cells have a thermometer sealed into the case which contains them. This case was packed in sawdust, and one of our own thermometers verified at Kew last November was placed in the sawdust. The thermometer in the cell was found on some five or six different occasions to read 0°·4 or 0°·5 below our own. The Kew correction for our standard is − 0°·16, at about 16°, the temperature of the observations. According to this there is a correction of about + 0°·3 required to the thermometer in the cell.

Making this correction, the following values were found for the excess of E.M.F. of Professor Ayrton's cell over our own reduced to the same temperature :—

Table XX.

Cells.	July 13.	July 14.	July 21.
Number.			
1	− 1·5	0	− 2
2	·5	1	− 1

The differences, it will be seen, are within the errors arising from uncertainty of temperature.

§ 33. *Cells set up by Dr.* Kahle *in Berlin.*

In July last four cells were brought to Cambridge from Berlin, by Dr. Lindeck. Two of these, Nos. 69 and 70, were cells of the pattern devised by Dr. Feussner and described by Dr. Kahle, ('Electrotechnische Zeitschrift,' July 22, 1892.)

The positive pole is a piece of amalgamated platinum sheet. This and the mercurous sulphate are contained in a porous pot. The outer vessel surrounding the porous pot contains saturated zinc sulphate solution and crystals of zinc sulphate. The negative pole is a rod of solid zinc amalgam, bent at right angles so that one part is vertical, the other horizontal. The vertical portion is surrounded by a tightly fitting tube of glass, the horizontal part is among the crystals, so that the effective portion of the zinc is always surrounded by saturated liquid.

The other two cells, Nos. 29 and 12, are H cells, of the form devised by Lord

RAYLEIGH. The cells had been compared with each other and with other standards before leaving Berlin, the differences being determined in hundred-thousandths of a volt.

Table XXI. gives the differences between these cells and our standards in hundred-thousandths of a volt.

TABLE XXI.

Date	July 26.	July 27.	July 29.
Temperature .	16°·1	15°·9	15°·9
Number.			
69	− 15	− 18	− 14
71	− 11	− 15	Taken away
29	− 36	− 35	− 36
12	− 39	− 38	− 39

In comparing these results with the numbers given in other tables, it must be borne in mind that the unit here is only one-twenty-fifth of that previously employed.

It appears then that the standard form in use at Berlin has a slightly lower E.M.F. than that of our standard, while the H-cells are distinctly lower, differing by nearly ·0004 volt.

Dr. KAHLE has made an important series of observations, 'Zeitschrift für Instrumentenkunde,' April, 1892, on the effect of impurities on the E.M.F. of an H cell, and has determined absolutely their E.M.F., and that of Dr. FEUSSNER's form of cell. On reducing his numbers to the units employed by us, we find for the E.M.F. of the FEUSSNER cell the value 1·4339 volt, and for that of the H-cell 1·4337 volt. The value obtained by us for the E.M.F. of our standard is 1·4342 volt. Thus Dr. KAHLE's experiments agree with our own in making the E.M.F. of our cells rather higher than those constructed by him, though the difference is small.

As we have already mentioned, the differences between the Cell No. 69 and the others were found at Berlin; the same differences can be obtained from our experiments. They are shown in the following :—

TABLE XXII.

Place of experiment.	Values of E.M.F. of		
	69–71	69–29	69–12
Berlin	– 2	29	29
Berlin	– 4	23	25
Berlin	– 4	25	26
Cambridge	– 4	21	24
Cambridge	– 3	19	20
Cambridge	. .	22	25

The differences between the cells at Berlin and at Cambridge are practically the same. Thus, we may fairly suppose they have not been affected by the journey.

Dr. KAHLE states that it is his experience that an H cell always has a rather lower E.M.F. than one with a porous pot put up with the same materials. On this point we have made no direct experiments.

§ 34. *Third form of the Board of Trade Memorandum.*

As experience has been gained in the construction of the cells, the Board of Trade Memorandum has been somewhat modified. We give it in its third form here.

The cells constructed in accordance with it are not readily portable, and may possibly in time get damaged by the accidental contact of the mercury and zinc. To avoid this the porous pot of the Feussner cell, or the cork diaphragm used by Professor CARHART, may with advantage be employed.

MEMORANDUM ON THE PREPARATION OF THE CLARK STANDARD CELL.

Definition of the Cell.

The cell consists of zinc and mercury in a saturated solution of zinc sulphate and mercurous sulphate in water, prepared with mercurous sulphate in excess, and is conveniently contained in a cylindrical glass vessel.

Preparation of the Materials.

1. *The Mercury.*—To secure purity it should be first treated with acid in the usual manner, and subsequently distilled in vacuo.

2. *The Zinc.*—Take a portion of a rod of pure redistilled zinc, solder to one end a piece of copper wire, clean the whole with glass paper, carefully removing any loose pieces of the zinc. Just before making up the cell dip the zinc into dilute sulphuric acid, wash with distilled water, and dry with a clean cloth or filter paper.

3. *The Zinc Sulphate Solution.*—Prepare a saturated solution of pure ("pure re-crystallised") zinc sulphate by mixing in a flask distilled water with nearly twice its weight of crystals of pure zinc sulphate, and adding about 2 per cent. of zinc oxide to neutralize any free acid.* The crystals should be dissolved with the aid of gentle heat, but the temperature to which the solution is raised should not exceed 30° C.; about 12 per cent. of mercurous sulphate treated as described in 4 should be added, and the solution filtered, while still warm, into a stock bottle. Crystals should form as it cools.

4. *The Mercurous Sulphate.*—Take mercurous sulphate, purchased as pure, and wash it thoroughly with cold distilled water by agitation in a bottle; drain off the water, and repeat the process at least twice.* After the last washing drain off as much of the water as possible.

Mix the washed mercurous sulphate with the zinc sulphate solution, adding sufficient crystals of zinc sulphate from the stock bottle to ensure saturation, and a small quantity of pure mercury. Shake these up well together to form a paste of the consistence of cream. Heat the paste, but not above a temperature of 30°. Keep the paste for an hour at this temperature, agitating it from time to time, then allow it to cool; continue to shake it occasionally while it is cooling. Crystals of zinc sulphate should then be distinctly visible, and should be distributed throughout the mass; if this is not the case, add more crystals from the stock bottle, and repeat the whole process.

This method ensures the formation of a saturated solution of zinc and mercurous sulphates in water.

Contact is made with the mercury by means of a platinum wire about No. 22 gauge. This is protected from contact with the other materials of the cell by being sealed into a glass tube. The ends of the wire project from the ends of the tube; one end forms the terminal, the other end and a portion of the glass tube dip into the mercury.

To set up the Cell.

The cell may conveniently be set up in a small test tube of about 2 centimetres diameter, and 6 or 7 centimetres deep. Place the mercury in the bottom of this tube, filling it to a depth of, say, 1·5 centimetre. Cut a cork about ·5 centimetre thick to fit the tube; at one side of the cork bore a hole through which the zinc rod can pass tightly; at the other side bore another hole for the glass tube which covers the platinum wire; at the edge of the cork cut a nick through which the air can pass when the cork is pushed into the tube. Pass the zinc rod about 1 centimetre through the cork.

Clean the glass tube and platinum wire carefully, then heat the exposed end of the platinum red hot, and insert it in the mercury in the test tube, taking care that the whole of the exposed platinum is covered.

Shake up the paste and introduce it without contact with the upper part of the walls of the test tube, filling the tube above the mercury to a depth of rather more than 2 centimetres.

Then insert the cork and zinc rod, passing the glass tube through the hole prepared for it. Push the cork gently down until its lower surface is nearly in contact with the liquid. The air will thus be nearly all expelled, and the cell should be left in this condition for at least 24 hours before sealing, which should be done as follows:—

Melt some marine glue until it is fluid enough to pour by its own weight, and pour it into the test tube above the cork, using sufficient to cover completely the zinc and soldering. The glass tube should project above the top of the marine glue.

The cell thus set up may be mounted in any desirable manner. It is convenient to arrange the mounting so that the cell may be immersed in a water bath up to the level of, say, the upper surface of the cork. Its temperature can then be determined more accurately than is possible when the cell is in air.

In using the cell sudden variations of temperature should as far as possible be avoided.

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* See notes at the end of the memorandum.

Notes to the Memorandum on Clark's Cell.

The Zinc Sulphate Solution.—The object to be attained is the preparation of a neutral solution of pure zinc sulphate saturated with $ZnSO_4 . 7 H_2O$.

At temperatures above 30° C. the zinc sulphate may crystallise out in another form; to avoid this, 30° C. should be the upper limit of temperature. At this temperature water will dissolve about 1·9 times its weight of the crystals. If any of the crystals put in remain undissolved they will be removed by the filtration.

The amount of zinc oxide required depends on the acidity of the solution, but 2 per cent. will, in all cases which will arise in practice with reasonably good zinc sulphate, be ample. Another rule would be to add the zinc oxide gradually until the solution became slightly milky. The solution, when put into the cell, should not contain any free zinc oxide; if it does then, when mixed with the mercurous sulphate, zinc sulphate and mercurous oxide are formed; the latter may be deposited on the zinc and affect the E.M.F. of the cell. The difficulty is avoided by adding as described about 12 per cent. of mercurous sulphate before filtration; this is more than sufficient to combine with the whole of the zinc oxide originally put in, if it all remains free; the mercurous oxide formed together with any undissolved mercurous sulphate is removed by the filtration.

The treatment of the mercurous sulphate has for its object the removal of any mercuric sulphate which is often present as an impurity.

Mercuric sulphate decomposes in the presence of water into an acid and a basic sulphate. The latter is a yellow substance—turpeth mineral—practically insoluble in water; its presence at any rate in moderate quantities has no effect on the cell. If, however, it is formed, the acid sulphate is formed also. This is soluble in water and the acid produced affects the E.M.F. The object of the washings is to dissolve and remove this acid sulphate, and for this purpose the three washings described in the memorandum will in nearly all cases suffice. If, however, a great deal of the turpeth mineral is formed, it shows that there is a great deal of the acid sulphate present, and it will then be wiser to obtain a fresh sample of mercurous sulphate rather than to try by repeated washing to get rid of all the acid.

The free mercury helps in the process of removing the acid, for the acid mercuric sulphate attacks it, forming mercurous sulphate and acid which is washed away.

§ 35. *Conclusion.*

We conclude, then, as the result of these experiments, that Clark cells put up at very different times and in very different manners have very approximately the same E.M.F.

1·434 volts at 15°,

and that they may very conveniently be used as standards of electromotive force.

× = Observations for Current.

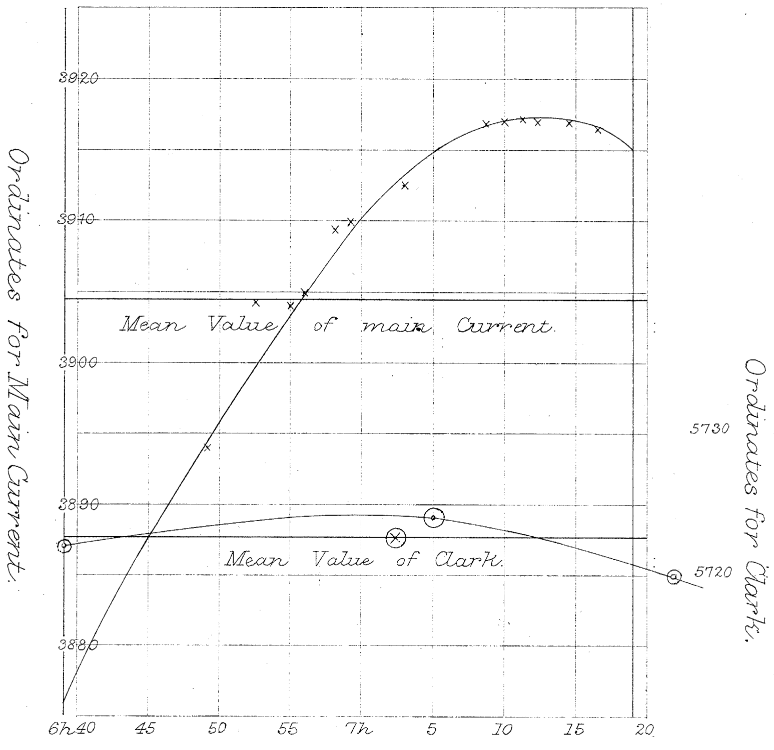
⊙ = Observations for Clark.

⊗ = Mean Value of Clark.

The Zeros from which the Ordinates for the Current and Clark respectively are measured are different.

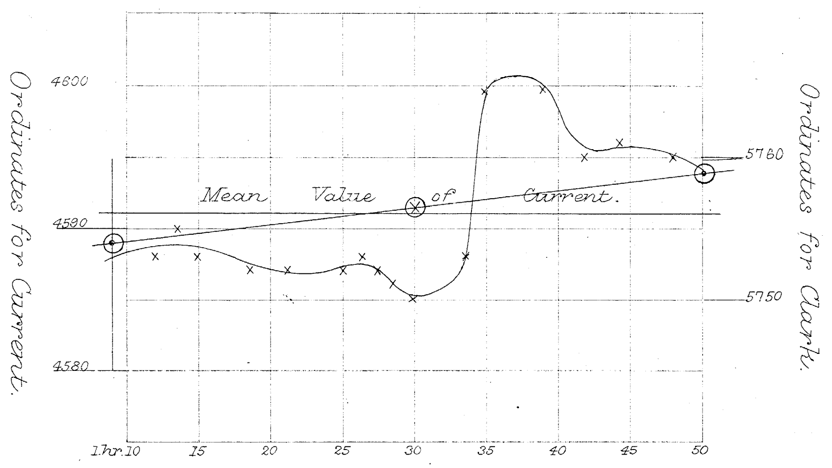
Mean Value of Current 3904·5.

Mean Value of Clark 5722·5.



Curve of E.M.F. July 31st

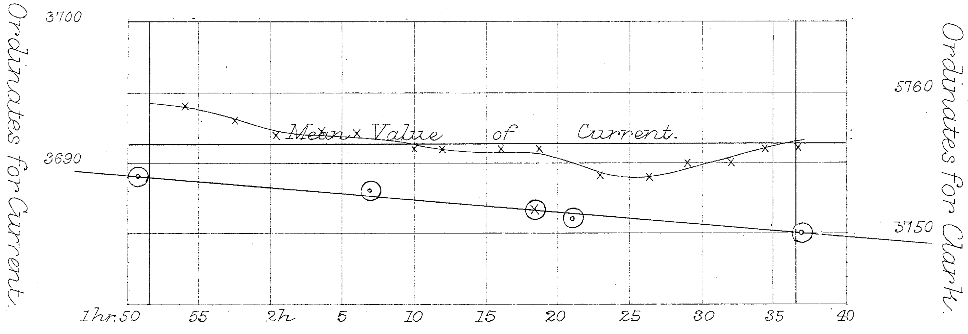
Mean Value of Clark 5756·5



Curve of E.M.F. Aug. 3rd

Mean Value of Current 3691·2.

Mean Value of Clark 5751·5.



Curve of E.M.F. Aug. 5th

West, Newman sc.