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T R A N S A C T I O N S :

On the Clark Cell as a Standard of Electro-Motive Force

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XVI. *On the CLARK Cell as a Standard of Electro-motive Force.**By Lord RAYLEIGH, F.R.S.*

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§ 39. The importance of a convenient standard of electro-motive force is now fully recognised. It gives the most available means of measuring currents, especially of large amount, and has been used for this purpose by several experimenters. I may refer to my investigation on the Constant of Magnetic Rotation of Light in Bisulphide of Carbon,* in which the currents were all measured by reference to a CLARK cell, whose value was originally obtained by absolute measurements and verified at intervals by the silver voltameter. CLARK cells are exceedingly convenient in use, and would doubtless be generally employed, could confidence be felt in their permanence, and in the equality of cells set up by different persons from the same recipe. To these questions I have given much attention; and the result of a large experience is very favourable to the trustworthiness of the cells, if reasonable precautions be observed in charging them. I believe that any one who takes the trouble to set up three or four cells and compares them occasionally, will be in possession of a standard of E.M.F. which he may trust to about $\frac{1}{1000}$ th part.

The present memoir is to be regarded as supplementary to that on the Electro-chemical Equivalent of Silver, and on the Absolute Electro-motive Force of CLARK Cells,† and the paragraphs are numbered accordingly. The total number of cells experimented upon is large. Of my own construction there have been about 60 of the ordinary kind (with solid zincs), and about 30 of the H-pattern (§ 28) with zinc amalgam. In addition to these some 40 cells made by others have been compared, with very interesting results to be given later.

Before entering into details it may be convenient to summarise the principal sources of error. The E.M.F. may be too high, (1) because the paste is acid, (2) because the paste is not saturated with zinc sulphate. The first fault tends to cure itself, and is rarely found after the cells are a month old. The second is the origin of the more serious discrepancies that have been met with in commercial cells. If the E.M.F. is too low, the cause may be, (1) that the cell has become dry, in which case the drop will probably be progressive, (2) the solution is *super*-saturated with zinc sulphate, (3) the mercury is impure.

* See *ante*, p. 343.

† Phil. Trans. Part II., 1884.

Believing that these cells are capable of affording standards of a high degree of precision, and that they ought to be in general use, I have gone into considerable detail as to the procedure which may be adopted. This may give the impression that the preparation is troublesome, but in reality the method that I propose is much simpler than those hitherto employed and thought to be necessary. To show how easy it is to set up these cells, I may refer to two large ones, contained in glass cylinders of about 4 inches diameter, and provided with wooden covers by which the electrodes are carried. Enough common mercury was poured in to cover the bottom, contact being made with it by means of a platinum wire sealed in a glass tube. The jar was then filled to a height of about 4 inches with saturated solution of commercial zinc sulphate with which some mercurous sulphate had been rubbed up in a mortar. The zinc electrode was cut from ordinary sheet metal, and was suspended horizontally near the top of the liquid by a projecting tail. After the first few weeks these large cells have never deviated from the standard by much more than $\frac{1}{10000}$, and have been found very convenient for certain purposes on account of their comparatively small resistance. They have also been used for preliminary comparisons with cells whose value was unknown, in which case there was danger of more current passing than is desirable to allow through delicate standards.

§ 40. The method followed for making the recent comparisons is the same in substance as that described in § 28. The use of a high resistance galvanometer gave a greater facility of reading, a change of $\frac{1}{10000}$ in the E.M.F. under measurement giving a motion of the spot of light which could be seen without a telescope from across the room.

The accompanying table (XIII.) gives the values of most of the older cells in continuation of that contained in the note to § 30 (p. 459). Cells (4), (8), (9) were, I think, left at Cambridge; (18) and (19) were observed at intervals during 1885, but the E.M.F. was found to fall. When about three parts per thousand too low, they were removed for examination, and found to be dry. The water had exuded, or evaporated, through cracks in the paraffin wax. The cells of the H-pattern, H_6 , H_{13} were broken in a manner to be presently explained. On the other hand some new cells of the H-pattern, a , b , . . . f are included. They are those referred to in the previous paper as having been fitted up by Mr. THRELFALL, and are more than a year old.

The agreement exhibited in Table XIII. is very remarkable. In many cases the cells may be depended on not to vary relatively more than 2 or 3 parts in 10,000, notwithstanding considerable changes of temperature. It is, indeed, doubtful whether even the whole of the small variations recorded are real. 1° C. influences the E.M.F. about 8 parts in 10,000, and differences of temperature of two or three-tenths of a degree may well have occurred, since the cells were variously mounted, and no particular precautions were taken beyond the avoidance of readings at times when the temperature of the room (immediately under the roof) was changing rapidly.

TABLE XIII.

	Jan. 2, 1885.	Jan. 26, 1885. 56°.	March 2, 1885. 52°.	April 7, 1885. 56°.	June 4, 1885. 71°.	June 29, 1885. 64°.	Aug. 14, 18, 1885. 63°.	Sept. 3, 4, 1885. 64°5', 62°5'.	Oct. 22, 23, 24, 1885. 57°, 57°, 56°.	Nov. 23, 24, 1885. 54°, 52°.	Dec. 26, 1885. 52°.	April 27,* 1886. 58°.
CLARK 1	1·0000	1·0000	1·0000	1·0000	1·0000	1·0000	1·0000	1·0000	1·0000	1·0000	1·0000	1·0000
" 5	1·0000	1·0002	1·0002	1·0002	1·0004	·9998	1·0000	1·0001	1·0001	·9999	·9999	·9999
" 10	1·0002	1·0000	1·0000	1·0000	1·0001	1·0000	1·0001	·	1·0002	1·0002	1·0005	1·0003
" 11	1·0002	1·0000	1·0002	1·0000	1·0003	1·0002	1·0001	·	1·0001	1·0001	1·0002	1·0000
" 12	1·0004	1·0002	1·0002	1·0001	1·0002	1·0002	1·0001	·	1·0004	1·0003	1·0006	1·0001
" 13	1·0000	·9998	·9998	1·0000	·9998	1·0000	1·0000	·	1·0000	1·0001	1·0003	1·0001
" 14	1·0000	1·0000	1·0000	·9999	·9998	1·0000	·9999	·	1·0000	1·0001	1·00·3	1·0000
" 15	1·0006	1·0005	1·0005	1·0002	1·0002	1·0003	·9998	1·0005	1·0006	·9999	1·0006	1·0007
" 16	1·0004	1·0001	1·0001	1·0002	·9998	1·0000	1·0000	1·0000	1·0001	1·0003	1·0005	1·0000
H ₅	1·0000	·9998	·9998	·9998	1·0001	1·0002	·9999	1·0001	·9999	·9999	1·0001	1·0001
H ₁₀	·9998	·9998	·9998	1·0002	1·0002	1·0002	1·0001	1·0003	1·0001	1·0003	1·0005	1·0003
H ₁₁	·9998	·9996	·9998	1·0002	1·0002	1·0002	1·0001	1·0003	1·0001	1·0003	1·0005	1·0003
H ₁₃	·9995	1·0003	1·0001	1·0002	1·0002	1·0003	broken	1·0001	1·0001	1·0003	1·0004	1·0004
a	1·0002	1·0000	·9999	1·0002	1·0004	1·0004	1·0001	1·0003	1·0003	1·0003	1·0001	1·0003
b	1·0002	1·0002	1·0000	1·0002	1·0004	1·0004	1·0001	1·0003	1·0001	1·0002	1·0004	1·0003
c	1·0000	·9998	·9998	1·0000	1·0002	1·0002	1·0000	1·0000	1·0000	1·0001	1·0004	1·0003
d	1·0000	1·0000	1·0000	1·0000	1·0002	1·0004	1·0001	·	1·0000	1·0001	1·0001	1·0003
e	1·0010	1·0004	1·0008	1·0010	1·0010	1·0010	1·0004	1·0009	1·0009	1·0003	1·0004	1·0003
f	1·0002	1·0000	1·0001	1·0004	1·0006	1·0006	1·0003	1·0004	1·0004	withdrawn	1·0004	1·0003

* Added since the reading of the paper.

It may be convenient to recall that cells 1, 5, were made in Oct., 1883; 10-13 and 14-19 in May, 1884; H_5 in March, 1884; H_{10} , H_{11} also in March, 1884.

§ 41. In cells of the ordinary type the principal source of weakness is imperfect sealing at the top, due to cracks in the paraffin wax. As pointed out by Dr. ALDER WRIGHT,* a better result is obtained if the whole cell be imbedded in a large mass of wax than when (as in my cells) the wax is applied merely inside the tube, above the cork sustaining the zinc. During the last year I have replaced paraffin by marine glue, which, so far as can be judged at present, may be relied upon to effect a complete seal. The procedure will be described presently more in detail.

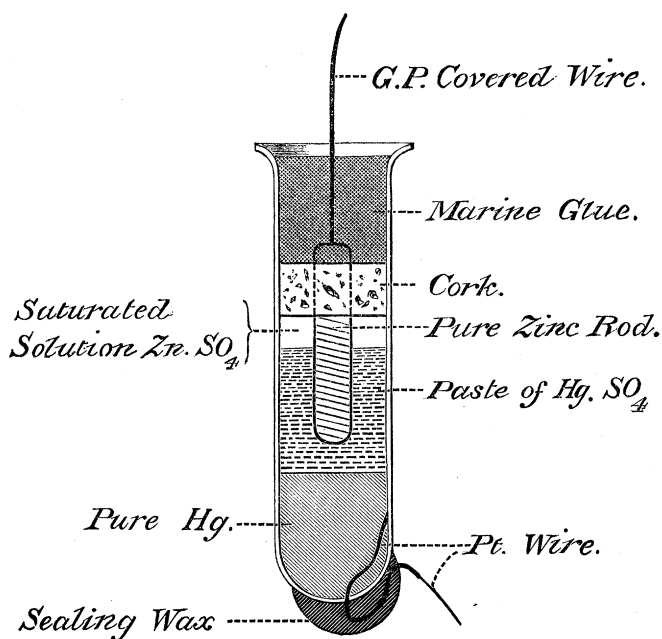
The cause of failure in the H-cells is of a different nature. Many of the earlier cells had been found to break in the amalgam leg, and the trouble was attributed to a hardening and expansion of the contents (§ 29). Such a hardening had, in fact, been observed in one or two cases. More recent experience, however, has proved that the cause must be looked for elsewhere, several cells having failed in which no trace of solid amalgam was to be found. Nevertheless the amalgam is the cause of the trouble, for out of a large number of breakages *not one* has occurred in the leg containing pure mercury. It would appear that some alloying takes place with the platinum wire in contact with the amalgam, and that this gradually extends itself with fatal results to the part of the platinum sealed into the glass, from which place the cracks are always observed to radiate. It is hoped that a cure will be found in a plan, adopted for some recent cells, of melting in a little cement (marine glue has been used) so as to protect from the amalgam the part of the platinum which lies nearest to the glass; but it is too soon to speak with certainty.

§ 42. The H-form lends itself to hermetical sealing, and at one time I anticipated advantage from this course. There is, however, such a large amount of spare liquid that there is no likelihood of trouble from desiccation, even if the corks allow a little evaporation. Indeed, by withdrawing the corks a fresh supply of liquid could be introduced at any time. It happened on one occasion that an H-cell to which a large excess of salt had been added, was so far crusted up next the metallic surfaces that it began to show signs of failing E.M.F., much as if it were going dry. The mass was so compact that no impression could be made upon it with a glass rod; but it was bored through with a steel reamer, when the E.M.F. at once recovered its normal value. In such cases the accessibility is advantageous, especially for purposes of experiment. It is well, however, to avoid such a large excess of salt as was present in this case. By alternate melting and crystallisation as the temperature rises and falls, there is a tendency to aggregation, of which the cell above referred to affords an extreme example.

In the construction of cells with solid zinc electrodes, I have fallen back upon a simplified pattern—nothing more in fact than a small tube with a platinum wire sealed through its closed end. See figure.

* Phil. Mag., July, 1883, p. 32.

The only objection to this form is that the cells cannot, without precaution, be supported from underneath. Most of mine are held at the centre by a spring (cut from sheet metal) against a piece of board mounted on its edge. In this case the copper electrodes are secured in sealing-wax to the wooden stand. For single cells, when portability is desired and convenience of immersion in water or ice, it is a good plan to enclose the whole in a rather long and narrow test-tube. A little cotton wool supports the cell and prevents it from shaking about laterally. The gutta-percha covered leads pass through a piece of cork inserted near the top of the test-tube, and a little marine glue poured over the cork makes all tight. In order to give mechanical support to the platinum wire, which is liable to break where it passes through the glass, the external application of sealing-wax is recommended—a precaution applicable also to the H-cells.



§ 43. In charging the cells the first step is to pour in sufficient *pure** mercury to cover the platinum effectively. The paste (of which more presently) is next introduced, with the aid of a small funnel, care being taken not to soil the sides above the proper level. The zincs, cut from rods of pure zinc, as supplied by HOPKINS and WILLIAMS, and not recast, 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

* Except when the contrary is stated, mercury distilled *in vacuo* has been used for CLARK cells. There is, I believe, a difficulty in purchasing mercury thus treated; but every physical laboratory should be provided with an apparatus for this purpose. That employed by me was distilled at Cambridge in an apparatus set up by Mr. W. N. SHAW.

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.

The marine glue is melted over the gas flame in a small pot or basin, and stirred, until uniform, with a small stick. It should be fluid enough to pour by its own weight. If necessary, a little benzole may be added, but the cement should be pretty hard when cold.

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 any other stage of the process of charging, is heat applied to the paste.*

§ 44. The earlier cells, prepared with paste, which was doubtless strongly acid, frequently gave irregular results for several weeks. Extreme cases are afforded by 15 and 16, which are shown by Table VIII. of the former paper to have been at first more than 2 per cent. too strong. Moreover, as appears from the continuation of this table in the notes (p. 459), it took nearly two months for these cells to settle down to their normal values. The cause of irregularity is to be sought rather at the mercury than at the zinc (or amalgam) electrode.

In order to examine this question, H-cells were charged with pure mercury and paste in both legs, and filled up as usual with saturated zinc sulphate solution. There should, of course, have been no E.M.F.; but the value of one of the cells was $\cdot 0041$ CLARK, and remained tolerably constant for several days. By stirring with a glass rod, the E.M.F. could be either increased or diminished. After some weeks the cells had come sensibly to zero, and would bear stirring (in one or both legs) without much disturbance. To another cell, which still showed irregularity, zinc carbonate was added. The E.M.F. was much reduced, and in a few days was scarcely sensible even on stirring.

When the paste is neutralised in the first instance with zinc carbonate, the irregularities are much reduced. Two cells thus prepared had an E.M.F. less than $\cdot 0001$ CLARK, and were scarcely affected by stirring. On Jan. 27, 1885, a piece of zinc wire was poked through the paste, so as momentarily to touch the mercury in one leg of one of these cells. A large E.M.F. was thus developed, which remained operative for half-an-hour or more; but on Jan. 28 the E.M.F. was only $\cdot 0003$ CLARK, and on Jan. 31 $\cdot 0002$ CLARK. It is clear that the mercurous sulphate has the property of freeing the mercury from the smallest contamination with zinc.

§ 45. In consequence of these observations more recent cells have been prepared with neutralised paste. This course has the advantage that the cells attain their normal values in a few days, sometimes within one day, of charging. So far as I can judge, however, there is no difference in the ultimate value whether the paste be acid

or neutral. In the former case the cell probably neutralises itself by dissolution of zinc, a certain amount of gas being liberated.

It is convenient to keep a stock bottle of saturated solution of zinc sulphate. This may be prepared in a flask by mixing distilled water with about twice its weight of crystals. A little carbonate of zinc is added to neutralise free acid, and 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 prepare paste, the bottle should be exposed to a gentle warmth for a few hours, and the solution should be 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 zinc sulphate 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 the mortar for two or three days, rubbing it up at intervals with additions of 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.

The performance of the newer cells has been satisfactory (one irregularity will be mentioned later), and the substitution of marine glue for paraffin wax promises a longer life. A large number of observations have been recorded, but it does not appear necessary to give them here in detail.

§ 46. I have been anxious to compare with my cells some prepared by others, and have to thank many physicists for the opportunity of doing so. Dr. ALDER WRIGHT was good enough to send me several of his cells, with which comparisons of especial value have been made. I shall have occasion to remark more at length upon the results obtained with these cells, and for the moment will only say that the difference between them and mine is under $\frac{1}{10000}$ th part. Cells prepared by Mr. THRELFALL (not those previously mentioned), by Dr. FLEMING, and by Prof. G. FORBES also agreed well.

Dr. FLEMING's cells, of which six remained in my hands, were at first irregular, and even now show somewhat larger variations than the best cells are liable to. The cause is, I believe, to be found in insufficient purity of mercury, as is suggested by

* It is usually found that on neutralisation the mercurous sulphate turns yellow, so that the paste presents ultimately somewhat the appearance of mustard. I do not know whether the change of colour is normal, or is to be attributed to impurity.

the appearance of the metallic surface. When the mercury is quite pure, the surface is as bright as in a thermometer bulb. I have instituted special experiments in order to ascertain the effects of impure mercury. On two occasions three cells have been charged alike in all respects, except that in the first vacuum-distilled mercury was employed, in the second ordinary mercury, and in the third mercury purposely contaminated with tin-foil (probably containing also lead). The results were not very distinct; but they indicate that impurity in the mercury is apt to depress the E.M.F. (e.g. by $\frac{1}{2}$ per cent.), and especially to make it irregular. I am disposed to attach great importance to purity of mercury, and believe it to be more essential than purity of zinc,* although I should not recommend the use of common zinc when the purer metal can be obtained so easily. Other cells have been prepared with mercury to which a little silver and copper (filings from a silver coin) were added. After the first week or two the E.M.F. of these cells was normal (to within $\frac{1}{1000}$ th part). It is probable that metals more oxidisable than mercury are removed from it by the paste, as certainly happens in the case of zinc.

§ 47. It has been abundantly proved by v. HELMHOLTZ, ALDER WRIGHT and other workers, that the E.M.F. of CLARK'S, DANIELL'S, and similar cells, rises as the zinc sulphate solution is diluted. In some such cells to be discussed presently (39, 40), the E.M.F. is about $1\frac{1}{2}$ per cent. higher than for a normal CLARK. Dr. HOPKINSON, some of whose cells have been compared with mine, writes that he is pretty clear that the worst irregularities of CLARK'S cells are due to the zinc sulphate not being saturated. A cell 2 per cent. in excess could be made right by simply introducing crystals of $ZnSO_4$. It is evident that sufficient care has not been taken in this respect in the preparation of cells sold to the public.

§ 48. In this matter of saturation there is another danger to be encountered, to which my attention was first drawn in connexion with some cells prepared with great care by Mr. MORTIMER EVANS, and left in my charge by Sir W. THOMSON. Of these, two were in practical agreement with mine; but the other eight, though in close agreement with one another, were too low (according to my standard) by rather more than four parts per thousand. And this state of things persisted without the smallest change for two or three months, during which tests were applied at intervals.

Being anxious to examine a phenomenon to which my experience had afforded no parallel, I opened carefully one of the abnormal cells (T_2) to the extent of withdrawing the zinc. My idea was that possibly the zinc solution was *supersaturated*, in which case the E.M.F. might be expected to be too low. Attached to the zinc, however, were found what appeared to be crystals of sulphate; but in order to be on the safe side, a few particles from the stock bottle were added to the cell, and the zinc was replaced. After the lapse of a few hours the E.M.F. was tested, *and was found to be normal*, as it has remained ever since.

* Of ten cells, prepared at the same time as a set to be used in series, five were made with pure zinc and five with common sheet zinc. No difference in the performance can be detected.

There was now little doubt but that the solution had been supersaturated, in the sense with which we are concerned. The presence of crystals is no evidence to the contrary, unless it can be proved that the crystals were those of the *normal, heptahydrated* salt.

At this stage I wrote to Mr. M. EVANS to inquire whether there was anything in the history of the cells that would account for the separation into two classes, and I was informed that all the cells had been prepared originally in the same manner. The mercury was twice distilled *in vacuo*, and in other respects the greatest care had been taken. When, however, the cells came to be tested, it was found that owing to contraction all but *two* were wanting in proper contact between the mercury and platinum, and that this contact could only be restored by remelting over a water-bath the whole of the paraffin wax in which the cells were imbedded. It was by this operation, no doubt, that the solution became supersaturated. The agreement with mine of the two cells which were not heated (one of them (T_3) is referred to later) is very satisfactory as showing that the great precautions exercised by Mr. EVANS lead to the same E.M.F. as I have obtained with far less trouble. I may add that a second abnormal cell (T_8) moved to equality with my standards on being opened.

§ 49. With a view to the better understanding of this matter I made myself acquainted with the beautiful researches of M. GERNEZ* upon supersaturation, conducted principally with solutions of sulphate and of acetate of soda; and have performed parallel experiments upon sulphate of zinc. A very strong solution of this salt prepared hot, and sealed up in a glass tube, will sometimes cool without any deposit. More often it throws down an abnormal (lower) hydrate. If in this condition the tube be heated pretty rapidly in boiling water, some of the salt dehydrates further to a powder (presumably mono-hydrated); if it be allowed to cool again the inferior crystalline hydrate reforms. However long the solution stands cold over this hydrate, it is still supersaturated as regards the normal hydrate, the minutest addition of which causes the supernatant liquid to become almost solid, with needles penetrating it in all directions. The experiment has been repeated many times with less strong solutions standing in open test-tubes, charged and preserved with the simple precautions indicated by M. GERNEZ.

It is evident that "supersaturation" is a term without definite meaning until further explained. GERNEZ has shown that a solution may be supersaturated with respect to one or both of two different hydrates, *i.e.*, will crystallise similarly on contact with the smallest fragment, and not supersaturated at all with respect to the anhydrous salt, the addition of which causes no effect. DE COPPET† has proved that the so-called supersaturated solution may be disposed to take up a further portion of anhydrous salt; as may, indeed, be inferred from previously known facts, since

* "Annales de l'école normale," t. iii., 1866, p. 163; t. v., 1876, p. 1.

† C.R. LXXIII., p. 1324, 1871. See also NICOL, Phil. Mag., June, 1885.

in general the anhydrous salt must tend either to leave or to enter the solution, and the former alternative is excluded by the observed behaviour on first contact.

§ 50. In view of the above facts we can hardly doubt that a CLARK cell, heated nearly to the temperature of boiling water and then cooled, would be likely to become supersaturated; but I thought it would be satisfactory actually to try the experiment. A normal cell of my own preparation and containing an excess of undissolved salt, was maintained for several hours at an elevated temperature, and tested after cooling. A temperature of 38° C. did not permanently alter the cell; neither did a temperature of 49°, nor one of 60°. But after an exposure to about 80° a permanent change set in. Immediately after cooling the value in terms of the standards was ·9914, but after one day's standing it settled to ·9943, close to which value it has since remained. It appears from the above that the cell probably requires to be heated sufficiently to decompose the normal hydrate, and not merely to bring all the immersed salt into solution. In the latter case there may well be solid particles within reach, which re-determine normal crystallisation on cooling.

A second experiment was tried with an old cell (*e* of Table XIII.) which contained a large excess of undissolved salt. This was of the H-pattern, which lends itself more conveniently to observation and experiment. On November 13 the cell was heated for several hours nearly to 100° C. After cooling a solid mass of crystals was to be seen over the metals in both legs, and it might have been supposed that the operation had been unsuccessful. On November 16, however, the E.M.F. was found to have changed (from about 1·0005) to ·9949, at which value it remained until November 25. On that day, at 5^h p.m. the corks were drawn. At 6^h no effect had been produced, and a fragment of the normal hydrate was dropped into each leg. At 6^h 45^m new crystals had formed, and the E.M.F. had risen to ·9996. A few hours later the E.M.F. was 1·0000, at which value it has since remained within 2 or 3 parts in 10,000. It was remarked that the crystalline deposit on contact with the normal hydrate was much less in amount than had been met with in experimental tubes with simple zinc sulphate. The explanation is probably that during the heating no complete diffusion of the salt was effected, so that after cooling supersaturation was limited to the lower layers. Both metals being at the bottom in this form of cell, the E.M.F. is independent of the condition of the upper parts.

It is worthy of note that all the "supersaturated" cells which I have tested are about 5 parts per 1000 too low. That they should give a definite E.M.F. is to be expected whenever the lower hydrate is formed. For the solution in contact with the lower hydrate is just as definite in composition as when it is in contact with the normal hydrate. It is, however, possible to have "supersaturated" solutions without formation of the lower hydrate, and then the E.M.F. would be indefinite. The deficiency may certainly be less than the 5 parts per 1000, and may probably be more in certain cases.

§ 51. In view of the possibility of error from under and over-saturation, the reader

may be inclined to ask whether it would not be better to prescribe a *dilute* solution for standard cells, as is conveniently done for standard DANIELL'S. One advantage attending this construction is (as will presently appear) a lower temperature coefficient. Again, we should be inclined to expect a more definite dependence upon temperature. In order to bring a saturated cell to its normal condition after warming (for example), it is necessary not merely that the whole of the contents should acquire the new temperature, but also that sufficient time should be allowed for *diffusion*. If the solution in contact with the zinc be weaker than corresponds to saturation at the altered temperature, the full loss of E.M.F. will not be experienced. In this respect the H-cells, in which the excess of salt rests upon the metals, would seem to have an advantage. But I cannot say that in practice I have met with the defect due to imperfect diffusion. Cells which have stood at 10° or 12° seem to acquire their new values after an hour or two's immersion in ice. The argument weighs, however, in favour of *small* cells, through which diffusion of temperature and matter can take place quickly. Such experience as I have had of cells prepared with dilute solutions, would not lead me to prefer them, even were there no difficulty in, or necessity for, a standardising. In the case of clear solutions, such as are used for DANIELL'S, the specific gravity is a convenient test of strength; but I do not see how a standard unsaturated paste could be accurately prepared without a good deal of trouble. Another objection to dilute solutions is the progressive alteration of E.M.F., due to evaporation, which must take place whenever the sealing is at all imperfect.*

In truth, there is no real difficulty in avoiding both under and over-saturation, if the experimenter will bear in mind the known properties of the materials with which he is dealing. The grosser errors, arising from the first cause, can only occur as the result of carelessness. As to the latter, it may be that supersaturation has sometimes entered as a consequence of excessive precautions against the admission of air. It cannot occur in the presence of the minutest fragment of the normal hydrate. Opinions may perhaps differ upon this point, but I am myself disposed to condemn the use of heat in charging the cells. If hot paste be brought into contact with hot mercury, and then closed hermetically, there must be some risk of supersaturation.

§ 52. The next question which I propose to consider is that of the temperature-coefficients of CLARK cells. My observations on cell No. 1 at Cambridge, § 36, gave for the proportional fall of E.M.F. per degree Centigrade in the neighbourhood of 15° the number ·00082, so that at t° C. we might take

$$E=1\cdot435\{1-\cdot00082(t-15)\}.$$

This number is in agreement with that found by HELMHOLTZ for saturated cells, but it differs seriously from the number (·00041) given by ALDER WRIGHT† also for

* ALDER WRIGHT. *Loc. cit.*, p. 33.

† Phil. Mag., July, 1883, p. 36.

saturated cells. These discrepancies have naturally led to the conclusion that the temperature-variations of CLARK cells are uncertain, and Dr. FLEMING has insisted upon the advantage in this respect possessed by the DANIELL.* If indeed it were a matter of chance whether the temperature-coefficient of a CLARK were '0008, or '0004, the utility of these cells as standards for delicate work would be seriously impaired. A glance, however, at Table XIII.† will show that such uncertainty need not exist. The results of March 2 and June 4 correspond to a difference of 19° F., or about 11° C., so that if one cell had the coefficient '0008, and another the coefficient '0004, the change of temperature would separate them to the extent of 44 parts in 10,000, whereas the greatest change observed (perhaps not due to this cause at all) is but 5 parts. Many observations on recent cells, made in ordinary course, point in the same direction. In one or two cases there has been an apparent rise at temperatures above 65° F., indicating a drop in the temperature-coefficient relatively to that of No. 1. I have attributed this to an insufficient excess of undissolved salt in cells prepared when the weather was cold, the result of course being a failure of saturation at high temperatures, attended (as will presently appear) by a fall of temperature-coefficient.

Being desirous of clearing up, as far as possible, any questions connected with the practical use of these cells as standards, I determined to supplement the former observations with special experiments at somewhat extreme temperatures, which should include as great a variety of constructions as possible. Most of the cells were so mounted that they could not well be tried at temperatures differing from that of the surrounding air, and I had to content myself with varying the temperature of the room by opening windows and burning gas. Care was taken that no great variation occurred within two or three hours of the comparisons. Under these circumstances tests were made of (1), (10) (Table XIII.); T₁ (one of the abnormal cells of Mr. M. EVANS'), T₃ (a normal cell of the same batch); W₃₁, W₅₉, W₆₂—three cells by Dr. ALDER WRIGHT; M₁₈₃, a cell sold by Messrs. CLARK and MUIRHEAD,—at temperatures from 47° F. to 69° F. These cells were all supposed to be saturated. There were also two prepared purposely with diluted paste—(39), (40). Besides these, two saturated cells of my own construction mounted in test tubes, which could be immersed in water or ice, were tested from 32° F. to 67½° F.

In order to obtain an absolute result we must have command of a standard independent of temperature-variations. At Cambridge I employed for this purpose a cell kept constantly in ice. The present observations were rather protracted, and I preferred to rely upon two cells (35), (38), mounted in test tubes and imbedded with a thermometer in a mass of sand, itself situated in an underground recess. The variations of temperature were here very small and readily determined, so that there

* On the "Use of DANIELL'S Cell as a Standard of Electro-motive Force," *Phil. Mag.*, Aug., 1855. It appears, however, to be, by a slip of the pen, that the coefficient for the DANIELL is represented as only $\frac{1}{50}$ of that of the CLARK. The numbers given lead to the ratio $\frac{1}{5}$.

† I must apologise for the Fahrenheit degrees.

was no practical uncertainty on this account. The variation of the two cells relatively to one another was less than $\frac{1}{10000}$ during the whole month of observation. (Table XV.)

TABLE XIV.—Value of Cells referred to No. 1.

Temperature. (Fahr)	Date, 1885.	(1).	T ₁ .	T ₃ .	W ₃₁ .	W ₅₉ .	W ₆₂ .	M ₁₈₃ .
47	Nov. 8 . . .	1·0000	·9957	..	·9991	·9991	·9993	..
49½	„ 2 . . .	1·0000	·9955	..	·9993	·9999	..	·9997
51	Oct. 31 . . .	1·0000	·9957	1·0001	·9996	1·0000	..	·9997
56½	„ 28 . . .	1·0000	·9957	1·0003
57	„ 27 . . .	1·0000	·9957	1·0001	1·0000	1·0000
58¼	Nov. 4 . . .	1·0000	·9954	..	·9992	·9992	1·0000	·9996
61	Oct. 30 . . .	1·0000	·9957	..	·9997	·9993	·9999	·9980
67	Nov. 27 . . .	1·0000	·9951	·9996	1·0001	·9996	·9997	1·0000
69	July 20 . . .	1·0000	·9957	·9998

From the results in Table XIV., reduced to No. 1 as standard, the reader will see that there is no distinct difference of coefficient. It is interesting to note that T₁ (which there is every reason to consider supersaturated) keeps its distance from No. 1. When I first thought of supersaturation, I regarded this agreement of temperature-coefficient as an argument on the other side, not at that time recognising the probable occurrence of the lower hydrate. But what will still more arrest attention is the agreement of Dr. ALDER WRIGHT's cells with No. 1. There are some irregularities, possibly dependent upon imperfect penetration of temperature through the masses of paraffin in which the cells are imbedded; but there is no distinct evidence of a lower coefficient, and certainly no such difference as that between ·0008 per degree Cent. and ·0004. The same may be said of M₁₈₃, which I received from Dr. ALDER WRIGHT.

§ 53. The absolute variations with temperature of (1), (10), (39), (40) are shown in Table XV., in which all the electro-motive forces are expressed in terms of (38) at 51° F., a small correction being introduced to allow for the 1° or 2°, by which the actual temperature of (38), (35), may have differed from 51°. The coefficients for (1) and (10) are almost identical. The observed values for (1) agree pretty well with the formula

$$\cdot 9970\{1 - \cdot 000425(t - 57)\},$$

as will be seen from the adjoining column calculated therefrom. This is in Fahrenheit degrees. The corresponding formula in Centigrade degrees is

$$\cdot 9970\{1 - \cdot 000765(t - 13\cdot 9)\}.$$

It appears, therefore, that the temperature-coefficient for these cells, including those of Dr. ALDER WRIGHT, is ·00077, and that the observed values are utterly irreconcilable with such a coefficient as ·0004.

TABLE XV.—In terms of (38) at 51° Fahr.

Temperature. (Fahr.)	Date, 1885.	(35) reduced to 51°.	(1) observed.	(1) calculated.	(10) observed.	(39) observed.	(39) calculated.	(40) observed.
°								
47	Nov. 8 . . .	1·0003	1·0013	1·0013	1·0014	1·0154	1·0155	1·0152
48 $\frac{1}{2}$	„ 1 (aft.) .	1·0003	1·0008	1·0006
49 $\frac{1}{4}$	„ 2 . . .	1·0003	1·0004	1·0003	1·0006	1·0150	1·0151	1·0149
51	Oct. 31 . . .	1·0003	·9996	·9996	·9997	1·0148	1·0147	1·0147
51	Nov. 7 . . .	1·0004	·9997	·9996	1·0000
51 $\frac{1}{2}$	„ 18 . . .	1·0004	·9993	·9993
52	„ 12 (morn.)	1·0004	·9994	·9991
52 $\frac{1}{2}$	„ 17 . . .	1·0004	·9994	·9989
53	„ 21 . . .	1·0003	·9988	·9987
53 $\frac{1}{2}$	„ 11 (even.)	1·0004	·9989	·9985
54	„ 20 . . .	1·0003	·9982	·9983
56 $\frac{1}{2}$	Oct. 28 . . .	1·0003	·9971	·9972	·9973	1·0133	1·0135	1·1032
56 $\frac{1}{2}$	Nov. 12 (aft.)	..	·9974	·9972
57	Oct. 27 . . .	1·0003	·9970	·9970	·9972	1·0134	1·0134	1·0133
57 $\frac{1}{2}$	Nov. 13 . . .	1·0004	·9970	·9968
58 $\frac{1}{4}$	„ 4 . . .	1·0004	·9964	·9965	·9963	1·0131	1·0131	1·0130
61	Oct. 30 . . .	1·0004	·9955	·9953	·9955	1·0125	1·0125	1·0125
67	Nov. 27 . . .	1·0004	·9928	·9928	·9927	1·0111	1·0113	1·0110

TABLE XVI.—In terms of (38) at 51° Fahr.

Temperature. (Fahr.)	Date, 1885.	(37) observed.	(37) calculated.	Temperature. (Fahr.)	Date, 1885.	(36) observed.	(36) calculated.
°				°			
32	Nov. 10 . . .	1·0051	1·0050	32	Nov. 11 (aft.) .	1·0067	1·0067
32	„ 11 (aft.) .	1·0050	1·0050	32	„ 11 (even.)	1·0066	1·0067
32	„ 11 (even.)	1·0051	1·0050	32	„ 12 (morn.)	1·0070	1·0067
40	„ 17 . . .	1·0028	1·0027	32	„ 12 (even.)	1·0068	1·0067
41 $\frac{3}{4}$	„ 21 . . .	1·0021	1·0022	40	„ 17 . . .	1·0038	1·0041
47 $\frac{1}{2}$	„ 8 . . .	1·0003	1·0003	41 $\frac{3}{4}$	„ 21 . . .	1·0028	1·0035
48 $\frac{3}{4}$	„ 12 (aft.) .	·9995	·9998	47 $\frac{1}{2}$	„ 18 . . .	1·0010	1·0013
49 $\frac{1}{2}$	„ 12 (morn.)	·9996	·9996	49 $\frac{1}{2}$	„ 13 . . .	1·0003	1·0005
49 $\frac{1}{2}$	„ 13 . . .	·9993	·9996	50 $\frac{1}{2}$	„ 2 . . .	1·0003	1·0001
50 $\frac{1}{2}$	„ 2 . . .	·9997	·9992	50 $\frac{1}{2}$	„ 10 . . .	1·0001	1·0001
52 $\frac{1}{2}$	Oct. 31 . . .	·9986	·9985	53	Oct. 31 . . .	·9992	·9991
52 $\frac{1}{2}$	Nov. 18 . . .	·9984	·9985	53	Nov. 18 . . .	·9992	·9991
57 $\frac{1}{2}$	Oct. 27 . . .	·9966	·9966	57 $\frac{1}{2}$	Oct. 27 . . .	·9970	·9971
57 $\frac{1}{2}$	„ 28 . . .	·9967	·9966	57 $\frac{1}{2}$	„ 28 . . .	·9971	·9971
61 $\frac{3}{4}$	„ 30 . . .	·9946	·9949	61 $\frac{3}{4}$	„ 30 . . .	·9950	·9952
66 $\frac{1}{2}$	Nov. 4 . . .	·9926	·9928	66 $\frac{1}{2}$	Nov. 4 . . .	·9931	·9929
67 $\frac{1}{4}$	„ 20 . . .	·9916	·9925	67 $\frac{1}{4}$	„ 20 . . .	·9923	·9925
67 $\frac{1}{2}$	„ 7 . . .	·9922	·9924	67 $\frac{1}{2}$	„ 7 . . .	·9925	·9924

For (39) and (40), prepared with unsaturated solution, the temperature-coefficient is exactly the half of that for the saturated cells. Reckoned in Fahrenheit degrees, it is ·00021, or in Centigrade degrees ·00038. The agreement with this value is shown by the column calculated from the formula

$$1\cdot0134\{1 - \cdot000212(t - 57)\}.$$

The coefficient $\cdot00038$ is so close to that given by ALDER WRIGHT, viz., $\cdot00041$, that one cannot help suspecting that the cells used by him for this purpose may have been unsaturated, or possibly supersaturated (without deposit of lower hydrate).

Over the above range of temperature a linear expression represents the E.M.F. sufficiently well. When, however, the values recorded for (36), and (37) for temperatures from 32° F. to $67\frac{1}{2}^{\circ}$ F. were plotted, a distinct curvature was apparent indicating a lower coefficient at the lower temperatures. Table XVI. exhibits the observed values, and (for comparison with them) numbers calculated from quadratic expressions. For (37) the expression is

$$\cdot9985\{1 - \cdot00037(t - 52\frac{1}{2}) - \cdot0000025(t - 52\frac{1}{2})^2\};$$

the equivalent of which in Centigrade degrees is

$$\cdot9985\{1 - 000666(t - 11\cdot4) - \cdot0000081(t - 11\cdot4)^2\}.$$

According to this, the change for one degree Cent. is the following linear function of temperature

$$\cdot000674 + \cdot0000162(t - 11\cdot4);$$

so that the temperature-coefficient ranges from $\cdot000489$ at 0° C. to $\cdot000813$ at 20° C. At 15° C. it would be $\cdot00073$.

For the other cell (36) the observed values of E.M.F. are pretty well represented by

$$\cdot9991\{1 - \cdot00042(t - 53) - \cdot0000028(t - 53)^2\},$$

from which are deduced the numbers in the column headed "calculated." In Centigrade degrees this becomes

$$\cdot9991\{1 - \cdot000756(t - 11\cdot6) - \cdot0000091(t - 11\cdot6)^2\};$$

giving for the temperature-coefficient at t° Cent.

$$\cdot000765 + \cdot000018(t - 11\cdot6).$$

At 15° the value from this formula is $\cdot00083$.

It would seem that these two cells have temperature-coefficients which differ sensibly. But this way of presenting the matter is apt to give an exaggerated impression. The difference in the coefficients indicates a separation of electromotive forces at the rate of $\frac{1}{10000}$ only per degree Cent., so that the whole relative change for ordinary indoor variations would not exceed $\frac{1}{1000}$ of the whole. It will be seen from Tables XIV., XV. that, through a more limited range of temperature, a large number of various cells are satisfactorily represented by the coefficient (intermediate between those just found) $\cdot00077$; and I believe that the adoption of this number* for cells with *saturated solutions* can lead to no appreciable error in ordinary use. For

* It should be mentioned that (*loc. cit.*) Dr. FLEMING found for a CLARK cell the coefficient $\cdot00082$ at 15° C.

very special purposes it will, no doubt, be desirable to protect standard cells from the larger temperature-variations, which is very easily done by keeping them in a cellar, from which well-insulated wires will convey the E.M.F. to any desired point. As to the absolute magnitude of the variations of E.M.F. with temperature, it may be worth while to recall that they are about the *double* of those experienced by German silver resistances.

§ 54. A good many special experiments have been tried with cells variously constructed, in order to elucidate as far as possible the behaviour of CLARK'S. Two of these, labelled H (1, $\frac{1}{2}$), H (1, $\frac{1}{4}$), were referred to in a short communication to the British Association at Montreal,* and have been observed at intervals since, with results which are, I think, of interest. In these cells, the legs representing the zincs were charged with a strong† but fluid amalgam of zinc and mercury; so that if the other legs had been charged with pure mercury and paste of mercurous sulphate, an ordinary CLARK would have resulted. This, however, was not done. No paste at all was used, and in place of pure mercury a dilute amalgam was substituted—in H (1, $\frac{1}{2}$) one obtained by diluting the strong amalgam with its own volume of pure mercury, and in H (1, $\frac{1}{4}$) one containing one volume of strong amalgam to three volumes of pure mercury. The cells were filled up, as usual, with zinc sulphate solution.

The electromotive forces, expressed as fractions of No. 1, are recorded in the adjoining table (XVII.). It is clear that the E.M.F. rises rapidly with temperature—something like 30 per cent. for 15° F. The large amount of this variation, and the fact of its taking place in the opposite direction to that followed by CLARK'S, are very remarkable.

TABLE XVII.

Date, 1834.	Temperature. (Fahr.)	H (1, $\frac{1}{2}$).	H (1, $\frac{1}{4}$).	Date, 1885.	Temperature. (Fahr.)	H (1, $\frac{1}{2}$).	H (1, $\frac{1}{4}$).
July 21 . . .	°	·0041	..	Jan. 2 . . .	°	·0033	·0083
„ 22	·0041	..	„ 14	·0031	·0081
„ 23	·0041	..	Aug. 3 . . .	63	·0044	·0095
„ 24	·0041	..	Sept. 5 . . .	63	·0042	·0095
„ 29	·0040	·0091	Nov. 6 . . .	52	·0034	·0083
„ 30	·0040	·0091	„ 12 . . .	56	·0039	·0086
Aug. 6 . . .	67	·0044	·0096	„ 27 . . .	67	·0044	·0093
Sept. 4 . . .	62	·0041	·0093	Dec. 2 . . .	51	·0034	·0084
Oct. 8 . . .	63	·0040	·0093				
„ 28 . . .	59	·0037	·0090				
Nov. 17	·0036	·0087				
Dec. 5	·0037	·0089				

It would appear that, apart from changes of temperature, the cells have retained their E.M.F. tolerably constant for more than a year and a half—a result which could

* B. A. Rep., 1884, p. 651.

† As to what is to be regarded as strong, more facts will presently be given.

scarcely have been expected, in view of the very small quantities of zinc which they contain.

If we diminish still further the proportion of zinc in the weaker amalgam, the E.M.F. increases; until, if we omit the zinc altogether, the E.M.F. may reach $\cdot 8$ or $\cdot 9$ CLARK. In this case, however, the E.M.F. is very unsteady.

On Feb. 18, 1885, a cell (F) of the H-pattern was charged with pure mercury in one leg, and in the other with an amalgam containing one milligram of zinc dissolved in 30 grams of mercury. No paste being used, the cell was filled up with saturated zinc sulphate solution. Under these conditions the E.M.F. was unsteady—about $\cdot 7$. On Feb. 23 some paste was added to the leg containing pure mercury, on which the E.M.F. became steady at $\cdot 939$ CLARK, even when the amalgam was stirred with a glass rod. On Feb. 28, E.M.F. = $\cdot 935$; on March 2, $\cdot 931$; on March 6, $\cdot 920$; on April 12, $\cdot 068$; and on Dec. 2, $\cdot 0003$.

Another cell (G) charged with pure mercury and paste in one leg had no zinc added to the pure mercury in the other leg, except such as it received by the passage for 3^m of the current from two large CLARKS, in whose circuit 1000 ohms of wire-resistance was also included. Under these circumstances, the deposited zinc should have been about $\frac{1}{10}$ mg. The resulting E.M.F. was $\cdot 923$, falling off from day to day, as in the case of (F). Nine months afterwards the value was $\cdot 0003$.

From these and other experiments it appeared that an astonishingly minute proportion of zinc in the amalgam was sufficient to give the cell most of the force of a CLARK. I had contemplated examining in greater detail the electromotive character of weak amalgams of known composition, when my attention was called by Prof. AYRTON to an interesting investigation by Messrs. HOCKIN and TAYLOR,* covering the same ground. In their cells zinc was opposed to the various amalgams; so that the circumstances were really the same as in the case of H ($1, \frac{1}{2}$), H ($1, \frac{1}{4}$), above discussed, the strong amalgam being equivalent to zinc. A few of their numbers may here be quoted. When the zinc was opposed to pure mercury, E.M.F. = 1.186 volt. (According to my experience this should have been uncertain.) The mercury being replaced by amalgams, the E.M.F. observed were as follows:—

Zinc 1 part, mercury	parts	Volts.
23,600,000	parts . . .	1.179
11,800,000	„ . . .	1.080
7,530,000	„655
5,900,000	„513
1,800,000	„214
400,000	„134
200,000	„124.

* "On the Electromotive Force of Mercury Alloys." 'Journal of Society of Telegraph Engineers,' vol. viii., 1879.

“Mercury alloyed with any number of metals takes the place in the scale of E.M.F. of the most electro-positive metal it may contain, if the amount of the electro-positive metal present is not less than about $\frac{1}{1000000}$ in weight of the mercury.”

§ 55. In order to obtain any stability of E.M.F. in these cells, it seems to be necessary that the mercury should either be alloyed with a sensible, though perhaps relatively very small, portion of zinc, or else protected with mercurous sulphate. With pure mercury without paste not only is the E.M.F. variable from hour to hour, but it can scarcely be said to be definite even at a particular time—that is, it may be altered by the passage of a very small quantity of electricity, such as should have no effect whatever upon a properly constituted cell. Sometimes when the galvanometer contact was made, a throw of the needle was observed, not followed by any corresponding permanent deflection, the cell in fact behaving like a charged condenser.

In the absence of paste a very small addition of zinc to mercury gives it a definite and tolerably permanent character. If, however, there be any mercurous sulphate, even though originally in another leg of an H-cell, the mercury is gradually repurified. To this cause is to be attributed the gradual fall to zero of the E.M.F. of the cells (F) and (G) above considered.

Indeed, the whole tendency of these observations is to suggest that the action of the mercurous sulphate may be secondary, rather than primary; so that if zinc could be opposed to really pure mercury, no mercurous sulphate would be needed in a CLARK cell. It may be, however, that in that case a minute quantity of mercurous sulphate would form itself spontaneously. In such cells as H (1, $\frac{1}{2}$) we are compelled to suppose that the chemical origin of the E.M.F. is the tendency of zinc and mercury to combine, or rather the tendency of two different amalgams to equalize themselves. There is here a close parallelism to the electromotive forces due to affinity of saline solutions of different strengths, manifested, for example, when an electrode of zinc is in contact with a strong solution of zinc sulphate, and the second similar electrode is in contact with a weak solution.

Before quitting this subject, I may mention observations on what was practically a CLARK cell, although prepared without zinc and without paste. On March 7, 1885, an H-cell (J) was charged with pure mercury in both legs, and filled up with zinc sulphate solution. A current from an external source of about $\frac{1}{400}$ ampère was then passed through it for $3\frac{1}{2}$ hours. The E.M.F. at subsequent dates were as follows:—

	CLARK.
March 9	·983
March 11	·980
April 9	·978
July 7	·973
December 12	·971

It will be seen that a tolerable approximation to a CLARK was obtained by this simple process. Zinc is thrown down upon the mercury in one leg, and mercury dissolved in the other by the passage of the current.

§ 56. The comparisons recorded in Table XIII. furnish abundant proof that there has been no special change in the E.M.F. of No. 1, but do not of themselves exclude the possibility of a general movement of the cells in one direction as the result of age, by which the relative values of cells of nearly the same date might remain unaffected. Comparisons with younger cells, indeed, go a long way towards negating this supposition; but considering that all the older cells had undergone a journey (from Cambridge to Terling), I thought that a re-determination of the absolute E.M.F., by means of silver, would be a valuable confirmation of their constancy.

With the assistance of Mrs. SIDGWICK, two such silver determinations were effected in August, 1885, as described in § 38. Reduced to 15°, the E.M.F. of No. 1 was found on August 15 to be 1·4541 B.A. volts, and on August 19, 1·4533, giving as a mean 1·4537 B.A. volts. The value found from absolute measurements in the autumn of 1883, and the spring of 1884, was 1·4542 (§ 36). That given (note to § 37) as the result of two experiments in Nov., 1884, is 1·4534; but a slight error has been discovered in the reductions leading to the latter number. By an oversight the factor 1·00041, necessary to correct for the slight heating of the resistance by the passage of the current (§ 33), was omitted, the effect of which omission is an under-estimate of the difference of potentials at the terminals of the resistance traversed by a known current, and consequently of the E.M.F. of the cell under test. This correction being introduced, the numbers will stand thus:—

TABLE XVIII.

Date.	E.M.F. of No. 1 at 15° C. in B.A. volts.
Oct. 1883 to April 1884 . . .	1·4542
Nov. 1884	1·4540
Aug. 1885	1·4537

The slight fall in these numbers has little significance; and we may regard the E.M.F. of No. 1 as having remained constant to within about $\frac{1}{2000}$ for nearly two years.

I believe that the E.M.F. of cells constructed with reasonable precautions, especially as to saturation, will rarely differ at ordinary temperatures by more than $\frac{1}{1000}$ part from

$$1\cdot454\{1 - \cdot00077(t - 15)\} \text{ B.A. volts,}$$

or (the B.A. unit of resistance being taken equal to ·9867 ohm)

$$1\cdot435\{1 - \cdot00077(t - 15)\} \text{ true volts.}$$

§ 57. In Table X., § 32, are given some comparisons with No. 1 CLARK of a standard DANIELL with equi-dense solutions of RAOULT'S pattern. As a mean at 16° C.,

$$\text{DANIELL} = \cdot 7703 \text{ CLARK} = 1 \cdot 1046 \text{ true volt.}$$

I have never succeeded in obtaining really good results with DANIELLS of any construction, variations in the conditions of the copper* rapidly altering the E.M.F. by two or three thousandths. The mean of a rather large number of comparisons in August, 1885, gives about $\cdot 7715$ CLARK at 16°, and this number was confirmed by further observations in December, 1885. The sp. gr. of the solutions was 1·101; the zinc was amalgamated, and the copper was freshly-coated electrolytically. The effect of variations in the condition of the metals and of the solutions are discussed by ALDER WRIGHT and by FLEMING.

Some observations have also been made with apparatus and solutions lent me by Dr. FLEMING, and arranged nearly according to the description published by him.† The variations observed with this form of DANIELL were smaller than with RAOULT'S, perhaps in consequence of the better protection of the copper solution from the atmosphere.‡ The mean value for 16° was about

$$\cdot 7674 \text{ CLARK} = 1 \cdot 1004 \text{ volt,}$$

in pretty good agreement with the value found by Dr. FLEMING himself. In correcting for the effect of a small variation of temperature, I have allowed only for the variations of the CLARK, assuming that of the DANIELL to be insensible.

[P.S.—May, 1886.—I have lately had the opportunity of comparing with mine five cells set up by Dr. A. MUIRHEAD, who has had great experience in these matters. All five agreed with my No. 1 to about one part in *ten thousand*. Dr. MUIRHEAD informs me that other cells, including one prepared by himself seven or eight years ago, agree closely with these.]

* It seems not unlikely that the greater part of the uncertainty of ordinary DANIELL'S might be got rid of by substitution of silver for copper. Silver *sulphate*, however, is not sufficiently soluble. But I have not made experiments in this direction, believing that the mercury of the CLARK cell is better still.

† Phil. Mag., August, 1885.

‡ In my experience the copper found its way to the zinc more readily than one would have expected. The amalgamated zinc became coated with a furry deposit, which struck a blue colour on solution in nitric acid and supersaturation with ammonia. In using RAOULT'S cells I have endeavoured to hold the copper in check by placing a loose strip of zinc in the connecting Y-tube.