AN HERMETICALLY SEALED TYPE OF CLARK STANDARD CELL.

BY H. T. BARNES.

OF the different types of Clark cell studied by the writer, a few hermetically sealed cells were made and briefly mentioned in another place.[1] The best of these cells, of the form known as the "sealed" cell, will be described somewhat in detail in the present paper. The advantage of a cell that can be completely closed by glass fusion is obvious. At the same time the cell should be moderately easy to construct, should embody strength and compactness, and should be perfectly portable. The present cell is primarily designed after the modified English Board of Trade model known as the B. O. T. "crystal" cell. It avoids the use of an amalgam button for negative electrode, which almost invariably ends by splitting the cell at the point where the negative terminal is fused through the glass, by the creeping of the amalgam along the wire. It includes the advantage of the "crystal" cell, *i. e.*, absence of diffusion lag, and has the extra advantage of being smaller and more sensitive. An important fact also is that the bulb of the cell containing the sensitive parts may be completely immersed in a water bath, or other form of thermostat, and at the same time is insulated thermally from the outside electrodes by the thick glass neck.

The arrangement of the cell will be best understood by reference to Fig. 1. In this the positive electrode is a platinum wire flattened at one end and amalgamated. The wire is enclosed in a glass capillary drawn from a small glass tube, shown in the figure, as the positive mercury cup. The negative electrode is a small zinc rod cast around a platinum wire and its enclosing glass capillary. This wire passes through the main fusion join *A*, and ends in the outer or negative mercury cup. As soon as the ingredients of the cell have been filled in through the open end, the final seal-

[1] H. L. Callendar and H. T. Barnes, Proc. Roy. Soc., 62, 117 (1897).

ing of the cell is made by quickly fusing the glass in the narrow neck, *B*. By placing a small quantity of mercury in the cups, terminals, pilot leads, or other connections can be inserted for comparison or test. When the cell is to be sent away or carried any distance, the mercury can be at once removed from the cups. The contents of the cell being in a firm mass, the cell may be kept in any position.

To construct the outer containing vessel, a glass tube, about one centimeter in diameter, is selected and cut about 15 or 16 centimeters long. This tube is drawn in the blowpipe flame at two places; one for the point of main fusion, *A*, Fig. 1, between 4 and 5 centimeters from one end, and the other *B*, so as to leave a bulb for the ingredients about 5 centimeters long. The restriction at *A* is to be left large enough to allow the zinc rod to pass through, while that at *B* should be large enough to allow of the insertion of the ingredients, through the remaining portion of the main tube not drawn down.

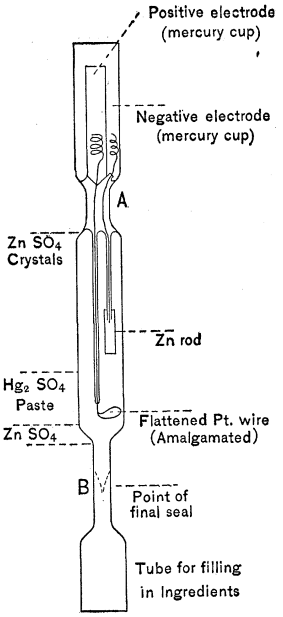

Fig. 1.

The positive electrode is made by drawing down a glass tube, of the same kind of glass as the main tube, 3 or 4 millimeters in diameter, into a firm strong capillary. This is shown at *P* in Fig. 2. The capillary should be long enough to reach from the main restriction, *A*, almost to the other restriction, *B*. A platinum wire, rolled flat for about a centimeter at one end, is passed through the capillary, and sufficient length left protruding into that portion of the tube not drawn down, which serves as the positive mercury cup. The capillary tube should be melted around the wire only at the end near the flattened portion. The amalgamation of the flattened end is done by heating red hot and cooling suddenly in pure mercury.

The negative electrode is made in the following way: a small mold of glass is constructed from a glass tube about 3 millimeters

in diameter and is filled with particles of absolutely pure zinc. These zinc particles are melted, and while melted, a platinum wire and a portion of its enclosing glass capillary is thrust in. On cooling and solidifying the glass mold is broken away, leaving the small zinc rod firmly attached to the capillary tube. This terminal is shown at *N*, Fig. 2. It should be long enough to reach from the seal *A* to the middle of the cell. Before inserting in the cell, the zinc rod should be scraped clean and bright and amalgamated by dipping into pure mercury upon the top of which a thin layer of dilute sulphuric acid is placed. By this means the zinc surface comes in contact with the mercury immediately after cleaning in the sulphuric acid, which is essential to ensure perfect amalgamation. After this process the rod should be most carefully washed free from every trace of acid and dried with filter paper.

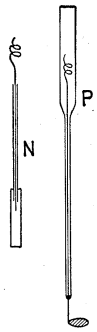

Fig. 2.

In making the main fusion, the two electrodes are placed in position by inserting them through the restriction at *A*, the positive electrode held central by means of small wedges, and the glass melted uniformly until it runs together around the two wires in a firm thick neck. The join is then carefully annealed to avoid cracking in the glass, which is liable to occur around the point where the positive mercury cup is sealed in, or at the point where the negative wire passes through. Before placing the electrodes in the cell, the ends of the wires for the mercury cups may be amalgamated.

In filling the cell, it is turned upside down and a small quantity at a time of moist zinc sulphate crystals pushed through the narrow neck by means of a small stiff glass rod. Once through the neck they can be shaken down into place. Crystals are added until the zinc rod is well covered. The paste, consisting of the usual mixture of pure washed mercurous sulphate and zinc sulphate crystals, is then pushed through in the same way. The paste should completely cover the flattened platinum wire. A few zinc sulphate crystals are then pushed through until they form a thin layer over the paste. The neck is then cleaned and dried as much as possible with filter paper, and fused together quickly in a small blowpipe

flame. Very little heat is imparted to the glass beyond the neck, and what is passed to the ingredients is taken up by the thin layer of zinc sulphate crystals, thus avoiding any decomposition of the mercurous sulphate. The small bubble of air left after fusing the neck allows of the slight expansion of the materials and guards against the bursting of the cell. The completed cell, as in daily use in this laboratory, is shown by the photograph in Fig. 3, about two-thirds natural size.

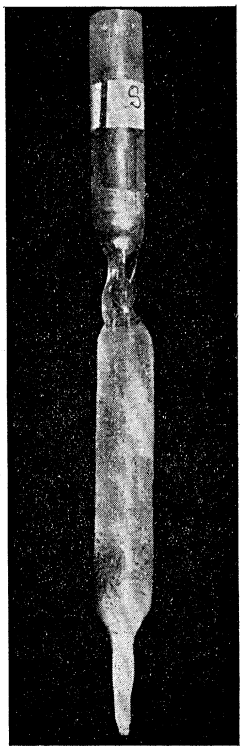

Fig. 3.

PREPARATION OF THE INGREDIENTS.

Mercury.—For amalgamation the mercury should be, when very impure, twice distilled in vacuum. When moderately pure, a single distillation is sufficient.

Zinc Sulphate.—The ease with which the very purest anhydrouszinc sulphate is obtained from any of the standard chemical manu facturers, makes it quite unnecessary to treat the solution with zinc oxide for neutralization, as recommended by the older processes. In order to obtain the heptahydrate crystals, the anhydrous salt is dissolved in water and a solution saturated at 30° C. prepared. While at 30° a small quantity of pure washed mercurous sulphate may be added, but it is not always necessary. It would depend on whether there was a trace of zinc oxide in the anhydrous salt. It, however, will do no harm and is immediately removed by filtering the solution in a water-jacketed funnel at 30°. The clear filtrate is cooled in melting ice, and the supernatant liquid poured off from the batch of crystals produced. Should a yellow turbidity appear in the process of cooling, it shows that the solution containing the mercurous sulphate has been heated to 35° or over. It is better to avoid the yellow turbidity altogether by not heating above 30°, but if present, the crystals may be remelted and the solution filtered un-

til completely removed. The crystals produced in the melting ice are put aside in a stock bottle.

Mercurous Sulphate.—The purest mercurous sulphate should be obtained and washed by decantation several times, with pure distilled water. After the final washing the salt is caught on a filter and drained. When moderately dry it is transferred to a mortar and an equal quantity of zinc sulphate crystals added from the stock bottle. The mixture is ground into a thick paste with some pure metallic mercury and transferred to a second stock bottle, dark-colored or otherwise protected from the action of the light by black paper.

TESTS AND COMPARSIONS.

From a careful study of the change of E.M.F. with temperature, for the various types of cells devised, the following simple formula in millivolts was found to fit the observations most closely between 0°C. and 30°C.

$$E_t = E_{15} - 1.200\,(t - 15) - 0.0062\,(t - 15)^2 \cdots \qquad (A)$$

The analogous formula finally obtained by Kahle reads

$$E_t = E_{15} - 1.19\,(t - 15) - 0.007\,(t - 15)^2,$$

which is in remarkable agreement. By formula (A) the total change between 15 and 0°C. is 16.60 millivolts, while between 15° and 30°C it is 19.40 mv. At 30° the actual observed change diverges from this simple parabolic formula, increasing more rapidly as the temperature rises to 40°, when the sudden change of hydration of the zinc sulphate causes the E.M.F. to rise and follow a different curve. The character of the temperature curve above 30° and 40° has been studied by the author, and the details of the experiments have already been published.[1] In that place it was shown that formula A, when corrected by the additional term

$$-0.00006\,(t - 15)^3 \cdots \qquad (B)$$

holds with great accuracy over the range 15° to 40°C. Above 40° the following expression represents the hexahydrate branch of the curve

$$E_t = E_{39} - 1.000\,(t - 39) - 0.007\,(t - 39)^2 \cdots \qquad (C)$$

[1] H. T. Barnes, Journ. Phys. Chem., 4, 1 (1900).

It appears probable that the divergence from the simple parabolic formula (*A*) above 30° is due to some action of the mercurous sulphate at the higher points, which does not appear below 30°, and is also the cause, as has been pointed out, for the lower value given by the Clark cell for the temperature of inversion of the heptahydrate and hexahydrate (38°.78C.), as compared with the value given by solubility determinations, which places it more nearly at 40°C.

A sufficiently clear idea may be obtained of the accuracy and sensitiveness of the "sealed" cell by reference to the author's paper above referred to, on the inversion of the hepta- and hexahydrates of zinc sulphate in the Clark cell. However, various other data are available and hitherto unpublished on this form of cell, and may not be out of place here.

In Table I. are shown comparisons on several cells made at different times, with different materials. The differences in their E.M.F. are expressed in millivolts.

TABLE I.

Cell.	Jan. 1896.	Feb. 1896.	Feb. 1898.	May 1898.	Jan. 1899.
S_1	−0.11	−0.13	+0.07	+0.02	+0.00
S_3	−0.10	——	——	——	——
S_4	+0.05	+0.03	——	——	——
S_5	+0.10	+0.11	+0.13	+0.12	+0.17
S_6	+0.01	——	——	——	——
S_7	——	+0.01	——	——	——
S_{10}	——	——	−0.02	——	——
S_{11}	——	——	——	——	−0.05
nS_{11}	——	——	——	——	−0.05
S_{12}	——	——	——	+0.27	——
S_{13}	——	——	——	−0.05	——

The differences are of the order of $\frac{1}{10}$ of a millivolt; with the exception of S_{12}, which was tested rather too soon after being set up. Owing to its removal from the laboratory with S_{13} shortly after, no further tests were obtained. It is probable, however, that it may have contained a slight trace of acid from the amalgamation of the zinc, which could only be removed by very vigorous means, such as short-circuiting the cell, or otherwise by the lapse of time. In

fact, one of the best methods of aging a cell and bringing it into a steady normal condition is by short-circuiting it with a copper wire for half an hour or so after setting up. The reads in Table I. show the variation from the mean of cells S_1 to S_6. Comparisons of cells S_{10} to S_{13} were made indirectly to cells S_1 to S_6 by comparison with five B.O.T. test-tube "crystal" cells that have been in the laboratory since 1895. A comparison of the means of the five sealed cells with the five crystal cells showed that the former exceeded the latter by only 0.08 millivolt. The five crystal cells have maintained their relative differences in a very satisfactory manner, as will be shown in another place.

During the progress of the author's experiments on the specific heat of water in terms of the international electrical units, two of these sealed cells were used and frequent comparisons made for a little over a year. These comparisons are given in Table II., and

TABLE II.

$S_5 - S_1$			$S_5 - S_1$		
Date of Comparison.	Difference in mv.	Temp. of Comparison.	Date of Comparison.	Difference in mv.	Temp. of Comparison.
Nov. 16, 1897.	0.10	15°	Apr. 12, 1898.	0.08	15°
Feb. 4, 1898.	0.06	"	" 20, "	0.10	"
" 22, "	0.02	16°	May 4, "	0.12	"
Mar. 1, "	0.03	"	" 5, "	0.10	"
" 3, "	0.02	14°	" 9, "	0.13	"
" 5, "	0.06	15°	" 14, "	0.11	"
" 9, "	0.05	"	" 23, "	0.10	20°
" 10, "	0.07	"	" 28, "	0.15	15°
" 11, "	0.04	"	June 10, "	0.10	21°
" 14, "	0.07	"	" 13, "	0.19	18°
" 16, "	0.06	"	" 17, "	0.12	"
" 23, "	0.07	"	July 23, "	0.10	20°
" 25, "	0.07	"	Sept. 10, "	0.16	19°
" 31, "	0.09	"	Oct. 14, "	0.17	14°
Apr. 2, "	0.06	"	Dec. 14, "	0.03	15°

will serve to show the way in which these cells may be relied upon to maintain their relative differences.

The variation in the difference between the two cells is so regular and consistent, never exceeding in the extreme case much more than 1 in 10,000, that over extended periods the difference can be

relied upon to one or two parts in 100,000. By taking sufficient care in the temperature and electrical measurements, this is about the order of agreement of this type of cell.

In regard to the temperature change and sensitiveness, some tests made on cell S_4 are given in Table III.

TABLE III.

Time after changing temp. of cell.	Total change of temperature.	Difference in mv. observed.	Diff. in mv. calculated by formula A.
5 minutes	15 to 0°C.	+15.90	+16.60
10 "	"	+16.44	"
60 "	"	+16.62	"
10 "	15 to 30°C.	−19.37	−19.40
30 "	"	−19.50	"

On returning to 30° from 50° C., the same cell showed a difference from its value at 15° of −19.62 mv. It is probable that had the cell been left at 30° in the first test longer than half an hour it would have shown a slightly larger difference. The total change between 15° and 30° by formula (*B*) is −19.60 mv., which is much closer to the observed value.

Table IV. contains tests made on cells S_4, S_5 and S_7, between 15°.36 and 23°.83 C.

TABLE IV.

Cell.	Total change in mv. observed.	Formula A.
S_4	−10.62	−10.62
S_5	−10.69	"
S_7	−10.62	"

Cell S_5 changed slightly more than the others, but the mean of the three cells will be a little in excess of formula (*A*), as is generally the case at the higher points.

The effect of a short circuit on one of these cells was shown by connecting the terminals of cell S_4 with a short, thick wire and obtaining comparisons of its E.M.F. during recovery after the wire was removed. In two and a-half minutes after short-circuiting for seven minutes, the E.M.F. was within three-tenths of a millivolt of

its original value. In ten minutes it was within two-tenths, and it had completely recovered in thirty.

For an account of the thermostats, potentiometer and temperature measuring instruments used in these tests, reference should be made to the author's earlier papers (in loc. cit.), where also the method of carrying out the experiments is described.

MACDONALD PHYSICAL LABORATORY, MCGILL UNIVERSITY, Feb. 14, 1900.

Fig. 3.