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XXXIV. *Variations in the Electromotive Force of the H-form of Clark Cells with Temperature.* By F. S. SPIERS, B.Sc., F. TWYMAN, and W. L. WATERS.

THE work described in this paper was intended as a completion of the investigation carried out some years ago by Prof. Ayrton and Mr. W. R. Cooper † on the effect of variations of temperature on the E.M.F. of the Board of Trade form of Clark cell. Their results showed that it was not possible, by applying the ordinary temperature-correction, to obtain the true value of the E.M.F. of the cell with a greater accuracy than 0·1 per cent. It was thought that the H-form of cell would show some improvement over the ordinary type in this respect; and this was confirmed by some results published recently by Dr. Kahle ‡. The experiments to be described in this paper were undertaken with the object of seeing how far this was correct, and in general to investigate the behaviour of this form of cell under variations of temperature. The experiments were carried out at the Central Technical College.

The tests were made on four cells set up in accordance with the specification issued by Dr. Kahle from the Reichsanstalt §. The cells were in every way alike ||, and were mounted

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† Proc. Roy. Soc. December 1895.

‡ *Zeitschrift für Instrumentenkunde*, August 1893.

§ 'Electrician,' vol. xxxi. p. 265, July 1893.

|| They were set up by Mr. Cooper, Nos. 1, 2, and 4 on 19th March, 1895, and No. 3 on 12th February, 1896.

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together inside a glass vessel in paraffin oil, and during the experiments they each underwent precisely the same treatment. The diameter of each of the two legs of the cell was about $\frac{3}{4}$ inch, and their length about one inch.

The method used for the determination of the E.M.F. was as follows. Current from a storage-cell traversed a potentiometer-wire in series with a resistance, the value of which was such that the fall of potential along the wire amounted to one ten-thousandth of a volt per centimetre-length. The cell to be tested was joined up in opposition to the standard, and the difference in their E.M.Fs. was balanced against the fall of potential along a certain length of the stretched wire.

The standard used in comparison consisted of one or other of two cells of the Muirhead type, which had been found to have an E.M.F. approximately constant during several years. The two cells were in one case, and during the experiments were placed in a thermostat in which the temperature could be kept constant to $0^{\circ}01$ C. The E.M.F. of the standard was determined absolutely by balancing it against the P.D. between the terminals of a resistance of known value of about three ohms, due to a current of about half an ampere passing through it. The resistance had been made specially for the purpose of manganin wire, wound upon an ebonite frame and immersed in paraffin oil. It had been previously aged by heating, and had assumed a steady value, as shown by comparison with standard manganin coils. The current was measured by a Kelvin centiampere balance, the constant of which had been frequently checked by means of a silver voltmeter. By this means the E.M.F. could be determined absolutely, correct to 0.0001 volt.

The thermostat consisted of an inner air-space, in which was placed the standard, surrounded by an outer water-bath which was heated by a gas-jet, the gas being automatically cut off when the temperature rose to a given value, and being allowed to come on again as soon as the temperature had fallen below that value.

In fig. 1, A B C are zinc vessels : A is the air-bath, containing the standard resting on cottonwool ; B the surrounding water-bath, closed at the top and containing the thermometer D ; C the enclosing jacket, between which and B the hot air from the gas-jet passes, heating the water-jacket on its way. D is an alcohol thermometer with a mercury-index F, which, on the expansion of the alcohol, is pushed up the narrow tube L, and electrically connects the two platinum wires f_1 and f_2 . J is the gas-jet for heating the water-bath ; K a baffle-plate over the gas-jet, to prevent the flame heating

the water-bath directly. E is an escape-tube, which serves to carry off some of the heat of the jet ; G is a little by-pass,

Fig. 1.

burning at the mouth of the tube E, and serves to relight the main jet when extinguished. M is an electromagnet ; H, its armature, is pivoted at S and weighted at P, and carries a platinum wire Q which dips into the mercury cup Q'.

When the temperature of the water-bath has reached a certain arbitrary value, the mercury-index electrically connects f_1 and f_2 , completing the circuit of the electromagnet M and the battery Z. The electromagnet being thus excited, attracts its armature H, which compresses the indiarubber tube T that feeds the main gas-jet J, between the brass piece N and the adjustable wooden block N', and so extinguishes the light. The water-bath now cools slowly till its temperature has fallen below the fixed value, and the contact is broken at f_2 by the falling of the mercury-index. When this happens, the armature of the electromagnet is released and pulled up at once by the weight P, the gas coming on again at the jet J ; some of the gas passing up the tube E is ignited at the top by the by-pass G, and then striking back, lights the main jet J, restarting the heating, and the cycle is repeated.

As it requires a less current to hold the armature down than it takes originally to attract it, the current circuit of the magnet is so arranged that when the armature is attracted it breaks the direct-current circuit at the mercury cup Q', and inserts into the circuit a resistance of 50 ohms, thus economizing the energy.

The temperature at which the cut-off acts can be adjusted several degrees by altering the distance which the wire f_2 projects down the tube L.

By carefully adjusting the size of the jet, the by-pass, and the height of the block N', we could keep the temperature of

the air-bath constant to $0^{\circ}.01$ C., the gas being cut off and coming on again about every five minutes.

To investigate the effect of temperature on the cells, it was necessary to be able to vary their temperature so as to get a uniform rise or fall. To effect this, some special form of heating-bath was needed. In its final form, this heating-bath consisted of an outer zinc bath, in which the vessel containing the Clark cells was placed, which was divided up by means of a number of partitions, reaching from the bottom of the vessel to above the surface of the oil. The oil was forced alternately under one partition and over the next, round the whole of the bath, and from the last compartment was drawn off into a separate chamber containing a heating-coil and a coil of lead tubing for an iced-water

Fig. 2.

circulation, and from this chamber it was again circulate round the compartments by means of a set of centrifugal vane

A (fig. 2) is the outer zinc bath, containing the oil, and divide

up into compartments by means of the zinc plates, *a, b, c, . . .* C, the inner glass vessel, contains the cells, and rests about one and a half inches from the bottom of the outer bath on the parts of the partitions *a, b, c, . . .* which reach to the centre. *g* is the separate compartment containing the heating-coil L, the coil of lead tubing K, and the centrifugal pumping-vanes V. The vanes V are directly coupled to a motor with a vertical shaft, this being found to be the most satisfactory way of driving them. The ring *h* separates the chamber *g* into two parts: in the upper, the vanes work and the oil is rotating; in the lower, the heating and cooling coils are placed, the oil in this part not rotating. *m* is a distributing plate under the hole in the centre of the ring *h*, which makes the circulating oil pass over the heating and cooling coils. D is a stationary guide vane which helps to deflect the rotating oil into the next chamber X.

The oil passes under the division *b*, over *c*, under *d*, over *e*, and finally under *f* into the heating-chamber *g*, where it passes over the heating-coil, and is sucked up through the hole in the plate *h*, and, being thrown out by the vanes V, is again circulated.

Fig. 3.

The circulation obtained by this means was excellent. When the bath was tested at a rate of change of temperature of 1° in eight minutes, there was found to be a maximum difference of temperature between any two points of the bath of $0^{\circ}2$; while at a rate of change of 1° in fifteen minutes, no difference in temperature was detected.

In the inner vessel containing the cells (fig. 3) the oil was

circulated by means of two sets of vanes ; the upper set, A, in the form of a screw-thread, was arranged so as to send the oil downwards on rotation ; the lower set, B, were radial near the centre, and at the outer ends curved so as to force the oil upwards. Thus, as the oil was forced downwards from the first set A, it was caught, and first sent outwards and then upwards by the second set B, thus producing a constant circulation. During our experiments the temperature in this bath was always uniform to at least $0^{\circ}02$ C.

Fig. 4.

employed as the potentiometer-wire. The resistance of this being known, the strength of current necessary to give a drop of potential of one ten-thousandth of a volt per centimetre length was calculated, and also the resistance required to be traversed by this current to produce a potential-difference between its extremities equal to the E.M.F. of our standard. The resistance R_1 was adjusted so as to be as nearly as possible equal to that value, and the deficit was found in terms of a length AP of the stretched wire. For example, suppose the resistance necessary to produce a potential-difference equal to the E.M.F. of our standard to be found by calculation to be 214.30 ohms. Plugs would be taken out of R_1 to the value of 214 ohms, and the point P on the wire would be selected such that the resistance of AP equalled 0.30 ohm. Then the mercury cups a, b and x, z being joined, the current sent through the wire by the storage-cell B was adjusted by means of the auxiliary variable resistance R_2 until the E.M.F. of the standard equalled the potential-difference between the points H and P. In this way the wire was rendered direct reading for any subsequent comparisons, one centimetre on the scale corresponding with one ten-thousandth of a volt. By joining the mercury cups a, b and x, z , the value of the current could be readily checked at any time during the experiment without interrupting the rest of the circuit. As a rule, very little variation was found

to occur. In this method we measure the difference of the E.M.Fs. of the cells on the stretched wire, and not the actual E.M.F. of the cell under test, consequently considerable variations of the current have very little effect on the result.

The cell under test was placed at T, and by joining the mercury cups *b, c* and *x, y*, this could be joined up with its E.M.F. in opposition to that of the standard; and then by moving the contact P, we could find a point such that the potential-difference between P and C equalled the difference in E.M.F. between the cell to be tested and the standard. If the difference between the E.M.Fs. was positive, then the point P lay on one side of the point C, while if the difference was negative, it lay on the other side.

To find how the changes in E.M.F. lagged behind those of the temperature, it was found best to subject the cells to a cycle of temperature, the temperature being first raised at a uniform rate through a certain number of degrees, and then cooled again at the same uniform rate to the original temperature. Supposing no lag to exist, the curve connecting temperature and E.M.F. would be the same for both rising and falling temperatures. But if there is a lag of short duration, *i. e.* not cumulative, then, provided that the temperature varies at the same rate throughout, two distinct curves, the second parallel to the first for the greater part of its length, will result, and will enclose an area between them. If there is any lag of a semi-permanent character, it will be shown by the curve not returning to its original starting-point till after a considerable time.

When we proceeded to take the cells through a cycle of temperature, we first of all determined absolutely the E.M.F. of the standard, which had been kept at a constant temperature for some days in the thermostat. The current for heating the cell-bath was then turned on, the required value of the current to give a certain rate of rise of temperature having been previously determined by experiment. The current in the stretched wire was then adjusted to its proper value, and the readings of the E.M.Fs. of the cells were taken every few minutes. The temperature of the cells was observed every five minutes and a curve plotted connecting temperature and time. The heating curve between time and temperature always gave practically a straight line, without readjustment of the current. When we started to cool our bath, we turned on the iced-water circulation full for the first few minutes, to get a sharp bend in the temperature and time curve, afterwards it was made to go much slower, and the flow required readjusting from time to time to keep the curve straight.

Considering that this adjustment was done purely by the method of trial and error, the curves obtained may be regarded as highly satisfactory. They approximate so closely to straight lines that it was thought unnecessary to reproduce them. In some of the cycles we cooled first and then heated afterwards, thus reversing the cycle. At the conclusion of each experiment the E.M.F. of the standard was again tested absolutely.

The accuracy of the method was all that was desired. The thermostat would keep the temperature of the standard constant to $0^{\circ}01$ C., and the temperature of the cell-bath was uniform to $0^{\circ}02$ at least. The difference in the E.M.F.s. could be read on the stretched wire to one hundred-thousandth of a volt. The E.M.F. of the standard never varied more than one ten-thousandth of a volt during an experiment, and in general it probably varied much less.

Three different rates of change of temperature were tried: 1° C. in seven minutes; 1° in fifteen minutes; and 1° in thirty minutes. A cycle generally lasted about five or six hours. The curves are plotted for E.M.F. and temperature, and, to avoid confusion, the curves for the different cells have been separated by displacing the origin of E.M.F. differences.

It will be seen that the curve connecting E.M.F. and temperature is not the same for both the rising and the falling temperatures in a cycle. As explained above, this indicates the existence of lag. The lag of E.M.F. at a rate of change of temperature of 1° in seven minutes is about four ten-thousandths of a volt; at a rate of change of 1° in fifteen minutes, it is about two-and-a-half ten-thousandths; at a rate of 1° in thirty minutes, it is about one twenty-thousandth of a volt. By this lag is meant half the difference between the E.M.F.s. given by the rising and falling curves for any particular temperature. If these lags are compared with those obtained for the B.T.-type of cell, in the paper above referred to, we see that the lag in the case of the H-form of cell is less than one quarter of that in the ordinary form. (See fig. 7. N.B.—The zero-lines on this diagram are purely arbitrary; the curves are merely for the purpose of comparison.)

The temperature at the close of a cycle was sometimes not exactly the same as at the commencement, hence the temperature-time curves are not closed. It is highly probable that if the temperature had been the same, the E.M.F. would have returned to its original value. On keeping the temperature constant at the end of the cycle, the lag passed off rapidly; at a rate of variation of temperature of 1° in fifteen minutes it disappeared in about ten minutes.

The probable reason for the superiority of the H-form over the ordinary form is that when the changes of temperature produce variations in the density of the zinc sulphate solution, the zinc amalgam, being at the bottom, is always in contact with a saturated solution, while in the B.T.-form we have the solution in contact with the mercury saturated, but that in contact with zinc will not be saturated till the whole of the paste has attained its equilibrium condition and again become saturated with zinc sulphate at the new temperature.

Thus in general it appears that in the H-form of Clark cell the lag is much less than in the B.T.-form, and that under ordinary conditions, when the rate of variation of temperature is not greater than 1° in half an hour, by applying the ordinary temperature-corrections we can obtain a result accurate to less than a ten-thousandth of a volt. If we wish to apply a temperature-correction for a greater rate of variation than this, we must either find the temperature-coefficient for variations at that rate from curves such as those given here, or else slightly diminish the ordinary coefficient. Subsequent experiments showed that if an H-cell were placed in a water-bath, which was heated through 3° or 4° as quickly as possible, then the E.M.F. of the cell would reach an approximately steady value as soon as the temperature of the bath, and by taking the temperature of the cell as being that of the bath, we could apply the temperature correction accurate to a ten-thousandth of a volt.

The two Muirhead cells used as standards in the above experiments were also taken through a single cycle at a rate of variation of temperature of 1° in fifteen minutes. From the curves (fig. 8) it will be seen that one of the cells is but slightly inferior as regards lag to the H-form, while the other comes about midway between the H and the B.T. forms. These two cells have been recently dismantled, and it was found that they were almost dried up and that the zinc sulphate had crystallized out over the top of the cells. They had thus practically become examples of Prof. Callendar's crystal cell*, and this probably accounts for their small lag. The cell which appeared the drier of the two had the larger lag.

Our best thanks are due to Prof. Ayrton and Mr. T. Mather for their many valuable suggestions and kind help, and to Mr. Cooper for the loan of the cells tested.

* Proc. Roy. Soc. October 1897.

APPENDIX.

Since the above investigation was completed, some experiments have been made to test whether the lag of E.M.F. observed was due to the lag of the temperature of the cell behind that of the bath or to diffusion lag. A B.T.-form of cell was made up in a tube 2 cm. diameter, and a thermometer inserted in a position similar to that occupied by the zinc. The cell was immersed in a water-bath so that the upper surface of the paste was about 2 cm. below the surface of the water. The temperature of the bath was then raised uniformly, the bath being kept stirred, and the temperature of the cell observed from time to time and compared with that of the water-bath. The lag of the temperature of the cell behind that of the bath was, at a rate of variation of temperature of 1° in six minutes, $0^{\circ}\cdot 15$; at a rate of 1° in fifteen minutes $0^{\circ}\cdot 10$; at a rate of 1° in thirty minutes less than $0^{\circ}\cdot 05$. The same experiment was tried with the thermometer half in the mercury and half in the paste so as to represent the condition of things in the H-form. The temperature lags in this position were found to be very slightly less than in the other.

Experiments were also made in which the cell at a temperature of 12° C. was placed in the bath at 30° C. and the bath stirred; the temperature of the cell was observed at different times. The observations showed that at the end of five minutes the lag behind the temperature of the bath was $0^{\circ}\cdot 10$, at the end of eight minutes practically zero. The temperatures in these experiments were observed accurate to $0^{\circ}\cdot 05$ C.

A Callendar crystal cell was tested in the same manner as the above and gave almost identical results.

It appears from these experiments that about half the lag of E.M.F. observed in the H-form of cell is due to the lag of the temperature of the cell behind that of the bath, and the rest to diffusion lag.

Hence in all experiments with Clark cells, where the temperature effects are likely to be serious, it is better to discard the B.T.-form of cell and use either Prof. Callendar's crystal cell, Prof. Carhart's modification of the B.T.-form, or the H-form. The Callendar crystal cell, in which the zinc rests in a mass of moist zinc-sulphate crystals, has a very small diffusion lag, but has the disadvantage that there is a possibility of particles of zinc falling and reaching the mercury. This fault is, however, eliminated in his inverted type. The Carhart cell, in which the solution is of constant strength, also possesses a very small diffusion lag, but it has

two serious drawbacks, firstly, an error of a few tenths of a degree in the temperature at which the cell is saturated makes an error of several ten-thousandths of a volt in the E.M.F., and, secondly, every time a current passes through the cell a certain amount of zinc is dissolved, so in time the solution becomes stronger. This point is of particular importance where the cells are used with condensers.

Fig. 5.—Curves connecting E.M.F. and Temperature. Rate of Variation of Temperature, 1° in 15 minutes.

Fig. 6.—Curves connecting E.M.F. and Temperature ; Rate of Change of Temperature 1° in 30 minutes.

Fig. 7.—Curves comparing the lag in the H-form of cell with that in the B.T.-form.

- A.** An average curve for Board of Trade cell. Rate of change of temperature, 1° in 15 min.
 (From paper of Prof. Ayrton and Mr. Cooper.)
B. H-form. 1° in 15 min.
C. H-form. 1° in 30 min.
D. H-form. 1° in 7 min.

Fig. 8.—Curves of E.M.F. and Temperature. Muirhead Cells. Rate of Variation of Temperature, 1° in 15 minutes.