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A TEMPERATURE-CONTROL BOX FOR SATURATED STANDARD CELLS

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ABSTRACT

In order to meet the need for a portable standard of electromotive force somewhat better than the unsaturated standard cell, a semiportable temperature-control box for a group of saturated cells was constructed, and is described here. The apparatus provides an adequate solution for the problem of maintaining a working standard of emf for those purposes for which the unsaturated cell is not good enough.

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I. INTRODUCTION

The unsaturated cadmium standard cell has been very generally used as a working standard of electromotive force, even in precise potentiometric measurements, having been preferred to the saturated cadmium cell principally on account of its portability and very low temperature coefficient.

It is commonly recognized that temperature gradients in the unsaturated cell may cause appreciable changes in its emf, but the effect known as "hysteresis" may also at times be an unsuspected but significant source of error. This hysteresis is a temporary change of emf, resulting from a change in the cell temperature, and tends to become more pronounced as the cells age. Its magnitude is uncertain and appreciable effects may persist for some days.¹

The saturated cell is more constant in emf but suffers from the disadvantage of having a rather large negative temperature coefficient, about 40 microvolts per degree C at 20° and nearly 60 microvolts per degree at 35° C. When used for precise work, either its temperature must be determined with considerable accuracy in order that corrections may be applied, or it must be placed in a thermostat, at some sacrifice of portability.

In precise calorimetry, a potentiometer is used to measure the power supplied to an electric heater, used to add definite quantities of heat to the calorimetric system. It was suspected that irregularities in the emf of unsaturated cells due to hysteresis may have been responsible

¹ J. H. Park. *Effect of service temperature conditions on the electromotive force of unsaturated portable standard cells.* BS J. Research 10, 89 (1933); RP518.

for occasional calorimetric errors, as large as 0.05 percent, and a convenient means of keeping saturated cells at constant temperature was therefore sought.

II. DESIGN AND CONSTRUCTION

The type of temperature controller having metal cases rather than a stirred liquid bath to distribute the heat was chosen on account of its simplicity and portability. The aim in the design was to control the cell temperature within $\pm 0.01^\circ \text{C}$ and to make it uniform to 0.001°C . Commercially pure aluminum was used for the cases on account of its lightness and high thermal conductivity. In this control box the temperature of an outer aluminum case is automatically controlled by a conventional mercury-in-glass thermoregulator. A second aluminum case, inside the first and thermally well insulated from it, contains the standard cells. The inner case will assume a temperature very nearly the time average of that of the outer case. The temperature oscillations of the inner case, resulting from the operation of the thermoregulator, can be attenuated to any reasonable degree by suitable choice of the heat capacity of the inner case and of the amount of thermal insulation between the two cases.

The box constructed provides space for five standard cells. The inner case is $3\frac{1}{2}$ inches long, $2\frac{1}{4}$ inches wide, and 4 inches deep inside. This case is a casting with walls $\frac{1}{4}$ inch thick and bottom $\frac{3}{8}$ inch thick. The cover, secured with numerous screws to improve thermal contact, is of sheet aluminum, $\frac{1}{4}$ inch thick. The inner case is spaced within the outer one with balsa wood $\frac{1}{2}$ inch thick on all six faces. The outer case is also a casting, with side walls $\frac{3}{8}$ inch thick and bottom $\frac{1}{2}$ inch thick. The cover of sheet aluminum $\frac{3}{8}$ inch thick is also secured with screws. The end walls of the casting are plane on the inside and cylindrical on the outside, the thickness at the edges being $\frac{3}{8}$ inch, and $\frac{3}{4}$ inch at the middle, this extra thickness providing space for a vertical hole $1\frac{1}{2}$ inch in diameter and 6 inches deep to accommodate the thermoregulator at one end and a smaller hole to accommodate a thermometer at the other end.

The outer case is insulated with a layer of balsa wood 1 inch thick on the sides and bottom, and 2 inches thick on the top. The pieces of balsa wood fit neatly into an outer wooden box. This box is long enough to provide a compartment at one end to contain a transformer, relay, and binding posts for the necessary connections. These accessories are mounted on a wooden panel which slides in vertical grooves in the sides of the box. The outside dimensions of the box are 8 by 13 inches, by 10 inches deep, and its weight, complete, is 22 pounds. A horizontal section of the control box is shown in figure 1.

The standard cells in the inner case were mounted on a simple support cut to appropriate shape from a piece of balsa wood. Connections to the cell terminals were made with no. 28 (0.013 inch) insulated copper wire, a length of about 4 feet being used for each terminal. About one-third of this length is in the form of a helix inside the inner case and another third is between the inner and outer cases. The wires were brought through the cases in smoothed saw cuts in the upper edges of the sides, and were insulated additionally with silk and glyptal lacquer, thus affording good thermal

contact with the metal cases, as well as adequate electric insulation (many thousands of megohms). These thermal tie-downs, and the considerable lengths of wire, reduce heat conduction from the outside along the wires to the cells to a negligible amount. Sheets of mica were placed on the surfaces of the aluminum cases, adjacent to the connecting wires, to protect them against accidental electrical grounding. Outside the outer case the wires were brought to binding posts supported on a hard-rubber strip set into the outer wooden box, the positive terminals being on one side of the box, the negative on the other.

The thermoregulator is of the adjustable mercury-in-glass type with a bulb 4 inches long and nearly $1\frac{1}{32}$ inch in diameter. The total length of the regulator is 8 inches. It fits rather closely into the hole in the outer case, and a coating of grease serves to improve the thermal contact. A part of the stem of the thermoregulator was

FIGURE 1.—Horizontal section of temperature-control box.

purposely left projecting above the outer aluminum case to compensate for changes in room temperature. The changes in room temperature alter the temperature of the projecting stem which in turn alters the temperature at which the regulator makes contact, in the proper sense to compensate for the displacement of its mean temperature due to the attendant changes in the relative lengths of the heating and cooling periods.

The heating resistor is no. 38 (0.004 inch) constantan and has a resistance of about 70 ohms. It is wound in about four turns, on the sides and ends of the outer aluminum case over silk fabric, the wire being spaced so as to distribute the heat as well as practicable. One turn is near the top edge and one near the bottom edge.

A small quick-acting alternating-current relay is used. It operates well on 12 volts at about 0.05 ampere although rated for 24 volts. Power for the relay and heater is supplied by a bell-ringing transformer rated at 50 watts, with secondary voltages from 4 to 24 in steps of 4 volts. The relay is operated on 12 volts and the heater

on 20. If the regulator should fail to shut off the current, the temperature of the cells would not rise more than 20 degrees above room temperature.

III. PERFORMANCE

Before the cells were installed, a bare resistance thermometer was temporarily mounted in the inner case. No oscillations traceable to the operation of the thermoregulator were detectable, although the sensitivity of the equipment used would have made it possible to detect changes of less than 0.001°C . The temperature oscillation in the outer case amounted to a few hundredths of a degree. The temperature of the inner compartment wandered slowly and irregularly, since the regulator did not maintain an entirely constant average temperature. The range of the wanderings was of the order of 0.01°C in the course of a week. A change of 15 degrees in room temperature produced no appreciable effect on the temperature in the inner case, showing that the compensation was adequate.

Four saturated cells were mounted in the control box at the end of March 1933. They were part of a group of 6 neutral cells made at the Bureau in November 1932. Redistilled new mercury was used for the positive electrode and in the amalgam, which was an electrolytic preparation containing 10 percent cadmium. The mercurous sulphate was also an electrolytic preparation. The cadmium sulphate was made by dissolving electrolytic cadmium metal in nitric acid, precipitating with redistilled sulphuric acid and heating, followed by four successive crystallizations. The glass blanks were of American soft glass with a minimum amount of sealing-in glass.

All 6 cells had been kept in an oil bath at 28°C up to the time the 4 cells were put in the control box, where their temperature was maintained at 32.8°C . A temperature of 35°C . would have been preferable for use in Washington during the summer, but as the effect of continuous exposure to temperatures above 28°C was not known, the more conservative selection was made. Table 1, taken from the record of tests of the cells, shows the results obtained.

TABLE 1.—*Electromotive force of cells in temperature-control box*

[International volts at 32.8°C]

Date	No. 773	No. 775	No. 776	No. 778
Apr. 7, 1933.....	1.017645	1.017642	1.017642	1.017642
Apr. 15, 1933.....	44	41	40	36
Apr. 22, 1933.....	40	39	38	27
May 6, 1933.....	35	36	34	22
May 20, 1933.....	31	34	33	21
Jan. 11, 1934.....	19	19	20	28
May 7, 1934.....	22	21	21	32

Each value recorded is representative of a group of observations made on several successive days. The data given above are not corrected for temperature, which in all cases was that maintained by the regulator.

The changes in emf of these cells, reported in table 1, are comparable with those of the remainder of the group which have been maintained at lower temperatures. Differences in emf from the

value for Weston normal cells at the respective temperatures, calculated on the basis of the international formula for the temperature coefficient of the Weston normal cell, are shown in table 2.

TABLE 2.—Comparison of changes in emf of cells in the control box with those of similar cells maintained at lower temperature

Cell number	Temperature	Differences from Weston normal cell		Total change
		Apr. 1933	May 1934	
		μv	μv	μv
773.....	In box 32.8° C.....	0	-23	-23
774.....	In oil bath 28° C.....	+3	-18	-21
775.....	In box 32.8° C.....	-3	-24	-21
776.....	do.....	-3	-24	-21
777.....	In oil bath 28° C.....	-1	-15	-14
778.....	In box 32.8° C.....	-3	-13	-10

Average change, 4 cells in box at 32.8° C..... -19
Average change, 2 cells in oil bath at 28° C..... -18

The changes shown in table 2 appear to be of the same magnitude and kind as those reported by Vinal and Howard² for a group of 14 neutral cells. The results therefore indicate that a temperature as high as 33° C has not been harmful to the cells.

Although the changes in the emf of the cells have been discussed in some detail, it is evident that the entire change would have been negligible, even in precise potentiometric measurements, under all ordinary circumstances. Only in case such a group of cells were used to maintain a reference standard of emf would it be necessary to take account of changes of the magnitude observed. It therefore appears that the portable control box, even at 33° C is adequate to control reference standards of emf to very nearly the precision attainable with the more elaborate baths in which the primary standards are kept.

When the prospective change from the international volt to the absolute volt shall have been made, the emf assigned to these cells will be about 1.0180 volts, a value within the range of the standard cell dials of most potentiometers now made. The low value is at present a minor inconvenience.

No provision was made for a thermometer to indicate the temperature of the inner case, as it was considered desirable to minimize the thermal connection between the two cases. It is possible, therefore, if the power fails for some time and comes on again an hour or two before observations are begun, that the thermometer in the outer case will indicate the proper temperature, while that of the cells may still be considerably too low. Such failure will be evident, however, if a synchronous electric clock of the type which stops when the power goes off is connected to the same line. Except on occasions when the power failed or the room temperature has exceeded 32° C, the regulator has operated continuously without failure for 17 months.

² Effect of glass containers on the electromotive force of Weston normal cells, BS J. Research 11,263(1933); RP588

IV. CONCLUSION

The temperature-control box provides an adequate solution for the problem of maintaining a standard of emf for those purposes for which the unsaturated cell is not good enough. A box of this type is ideally adapted for controlling the temperature of any small apparatus in which little or no heat is developed. A similar control box, much smaller in size, has been used successfully for nearly 2 years to control the temperature of the coils of a Wheatstone bridge for resistance thermometry, where the maximum power developed in the coils is a few milliwatts.

We are indebted to Geo. W. Vinal, for the four very excellent cells used as well as for the test data and comparisons showing their performance.

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