D.C.
SECTION

THE CONSTRUCTION AND CHARACTERISTICS OF STANDARD CELLS

BY

GEORGE D. VINCENT

The Construction and Characteristics of Standard Cells*

GEORGE D. VINCENT†

INTRODUCTION

IN order to maintain standards of the electrical units, two of the three quantities interconnected by Ohm's Law must be represented by stable reference standards. The best standard of EMF now known is the cadmium standard cell. The saturated cadmium standard cell, carefully made and maintained, has a reproducibility and stability in the order of one or two ppm, which is about one order of magnitude better than the accuracy at present attainable in the measurement of the absolute dimensions of the electrical units. Probably in the not-too-distant future, refinement in the determination of the electrical units in terms of fundamental standards, or of a natural constant, will require even more stable standards of reference.
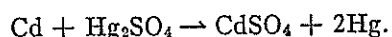
The history of the development of standard cells has been adequately covered by Wolff and Waters [1], Eppley [2], and Vinal [3].

TYPES OF CADMIUM STANDARD CELLS

Two forms of the cadmium standard cell are in general use: the saturated and the unsaturated. Each type is usually made in an H-shaped glass vessel, with a platinum lead wire sealed through the lower end of each limb. Efforts have been made from time to time to improve the form of the vessel, but to date no form representing any radical departure has been generally adopted.

The cell consists of a mercury cathode in the bottom of one limb, depolarized by a layer of mercurous sulfate immediately above, and a cadmium amalgam anode in the bottom of the other limb. The electrolyte, an aqueous solution of cadmium sulfate, fills the tube to above the level of the top of the cross arm.

The distinction between types arises from the condition of the electrolyte. In the saturated cell, an excess of solid crystals of $3CdSO_4 \cdot 8H_2O$ in the electrolyte space and in the depolarizer assure that the solution will be saturated at all temperatures. A simplified representation of the cell reaction is:

$$Cd + Hg_2SO_4 \rightarrow CdSO_4 + 2Hg.$$

The cadmium is removed from and the mercury deposited on the amalgam. As long as the amalgam is of such constitution that it has both a solid and a liquid

phase present, the EMF remains constant. The mercurous sulfate consumed results in a very slight diminution of the large excess of the solid depolarizer paste mass, and the cadmium sulfate produced must appear as solid crystals, adding slightly to the large excess. The electrolyte remains saturated. Therefore, as there is no qualitative change in the materials of the cell in any way that affects the EMF, the saturated cadmium standard cell has great stability over many years.

The change in concentration of the saturated electrolyte with temperature, however, requires correction of the assigned value of EMF for changes in temperzture. To avoid the necessity for such corrections or temperature control, the unsaturated form is very extensively used as a laboratory or industrial standard, when an accuracy of 0.01 per cent will suffice.

In the unsaturated cell, the electrolyte is slightly diluted. No excess of solid cadmium sulfate is present. It has been found that the temperature coefficient of EMF of a cadmium standard cell with an electrolyte of such concentration that it would be saturated at 4°C is very nearly zero [4]. The EMF of such a cell does not vary from its 25°C value by more than 0.005 per cent over the range from 4°C to 40°C. However, the cadmium sulfate produced in the cell reaction increases the concentration of the solution, resulting in a decrease in the EMF of the cell. The unsaturated form of the cadmium standard cell therefore does not lend itself well to use as a standard of reference over periods of many years, but must be compared from time to time with some reliable bank of saturated standards. Further discussion of the decrease in EMF of unsaturated cells appears below under the effects of temperature.

Nearly all standard cells made today have "acid" electrolytes; that is, free sulfuric acid has been added to the electrolyte. How much acid is added depends upon the type of cell, the materials used in the cell, especially the glass and the plugs, and the judgment of the manufacturer. Too much acid encourages gassing on the anode; too little results in cells with high hysteresis. Probably the range 0.01 N to 0.1 N with respect to H_2SO_4 includes all the commercially produced cells.

Acid lowers the EMF of the cell. Several formulas for relating the acid concentration and the change of EMF in standard cells have been published [5]–[7]. All are in good agreement over the short range of acidities used in standard cells. The most convenient for practical workers are Obata's,

$$\Delta E = - 855X,$$

in which ΔE is the change in EMF in microvolts and X is the normality of the acid in the saturated electrolyte of the cell, and the NPL formula [8]

$$\Delta E = - 615X$$

with ΔE as above and X the normality of the solvent before saturation.

MATERIALS

The chemicals required in a cadmium standard cell are water, sulfuric acid, mercury, cadmium, mercurous sulfate, and cadmium sulfate. Each of these materials can be prepared with a very high degree of purity.

Mercury

Conventional methods of purification of mercury—washing, electrolysis and distillation—are adequate, if carefully controlled. The Hulett method of distillation in a stream of air is more efficacious than distillation in vacuo [9].

Cadmium

As obtained commercially, cadmium often contains zinc, lead, thallium, manganese, silicon, and copper. With the exception of zinc, these impurities are all removed by distillation in vacuo, a single distillation usually sufficing to bring the 99.99 per cent commercial cadmium to, or nearly to, spectroscopically pure. Zinc, the exception, is reduced by each succeeding distillation, but choice of an essentially zinc-free cadmium to start, through analysis of the raw material, is the more convenient and economical approach.

Mercurous Sulfate

The depolarizer can be prepared in a variety of ways. The electrolytic method, essentially as described by Wolff and Waters [1], is probably used by all present-day manufacturers. The purity of the product is dependent upon the purity of the mercury, sulfuric acid, and water used.

Necessary characteristics of the mercurous sulfate as a depolarizer for standard cells are:

1) It must be the normal, unhydrolyzed salt.
2) It must be free of the mercuric salt.
3) The grain size must be greater than 3 microns.

The first condition requires that the mercurous sulfate be prepared, washed, and stored under strong sulfuric acid (*e.g.*, 6 N).

The second condition is maintained by the excess of metallic mercury in finely divided form, which is distributed throughout electrolytically produced mercurous sulfate. In addition to serving as the reducing agent in the mercurous sulfate, the metallic mercury also increases the conductivity of the depolarizer paste. It is necessary to protect the mercurous sulfate from contact with oxidizing agents, including atmospheric oxygen.

The third condition is met by digesting the mercurous sulfate at 100°C in sulfuric acid for several days, which results in the solution of the smallest grains and in precipitation upon the larger grains. The very fine grains of mercurous sulfate (under 3 μ long) cause irregularities of EMF [10]–[11].

Mercurous sulfate is light sensitive, changing at room temperature in light through tan and grey-brown to, finally, very dark brown or black. It is not so sensitive that it cannot be exposed for considerable periods, say a half hour, in rooms lighted by daylight, as long as direct sunlight is avoided. Very long exposure, running to many hours, to ordinary room illumination levels of incandescent lighting does not appreciably affect mercurous sulfate either in appearance or performance. Exposure to fluorescent lights must be limited the same as exposure to daylight.

Cadmium sulfate is obtainable from suppliers of high-quality chemicals in purity exceeding the reagent chemical specifications of the ACS. Unfortunately, manganese content is not specified therein. If cadmium sulfate of the ACS reagent grade has a manganese content below 1 ppm, one or two recrystallizations from water solution are sufficient to purify it for standard cell use. With careful selection of the commercial material, based upon spectroscopic analysis, it is sometimes possible to use reagent grade cadmium sulfate as purchased for the less precise types of cells. In recrystallizing cadmium sulfate, the maximum temperature permissible is 43.4°C, above which the monohydrate, $CdSO_4 \cdot H_2O$ will form [13]. The stable crystal at room temperatures, which must be used in standard cells, has the formula $3 CdSO_4 \cdot 8 H_2O$.

Sulfuric acid needs no special commentary here. Many sources exist for the purchase of very high purity sulfuric acid, which is adequate for use in standard cells.

Water must be purified for use in standard cells, the degree depending upon the requirements of the cells. A careful single distillation of ordinary tap water yields a product sufficiently pure for use in unsaturated standard cells, which are not expected to have accuracies better than 10 ppm or to have useful lives measured in decades. On the other hand, saturated cells for use as highest-grade standards over many years are customarily made with water that has been purified by redistillation until the metal ion impurities have been reduced to the same extent as in "conductivity water." Since the electrolyte system is always definitely acid, no elaborate precautions against CO_2 are required, but energetic bubbling with nitrogen is necessary to eliminate dissolved oxygen from water which is to be used in preparation of the electrolyte.

Glass is used to fabricate the blank, or vessel which contains the materials of the cell. Nearly all glasses are, to a greater or less extent, soluble in aqueous solutions, and act as neutralizers of free acid as they dissolve [14]. This has given rise to work with blanks of Pyrex and pure quartz [15], all of which have had limited success.

In addition to the difficulty of sealing lead wires through the glass, and of closing the blanks when made of high melting point glasses, there is also the possibility that the mercury reacts with high silica glasses. It is stated that Pyrex glass is less suitable than soda lime glass for bottling high purity mercury, due to the formation of a scum resulting from a mercury-silica reaction [16].

At any rate, many of the best cells made to date have been in blanks of soda lime or normal glass. Perhaps the best material will be found in one of the very inert organic plastics, such as the tetrafluorethylenes. Some thought has already been directed to plastic cell vessels [17]. Tests at The Eppley Laboratory have demonstrated that methacrylate, styrene, ethylene, and tetrafluorethylene polymers all give good promise of being satisfactory materials for use in standard cells. Vinyl and melamine polymers, when used in standard cells, give rise to excessive hysteresis and decreasing EMF's.

Cork, in the form of a washer, is used in many unsaturated standard cells as a plug to hold a fabric septum in place, to prevent movement of the electrode materials when the cell is moved or inverted. There is no doubt that the organic acids present in cork, as they leach out into the electrolyte, cause serious disturbances of EMF [18]. By careful preparation, however, the soluble materials are practically completely removed and with free acid in the electrolyte, as is always the case in modern unsaturated standard cells, the effect of cork is reduced to negligible for the first few years of cell life. The method of removing soluble materials from cork varies in important details among individual manufacturers, but is based in general upon leaching by long immersion in boiling water.

MOUNTING OF CELLS

Saturated cells are mounted together, usually in groups of from three to six, for convenience in handling and in making connections in constant temperature environments. The number of cells in the group is a combination of necessity and economy. Since saturated cells serve, in any particular laboratory, as the primary standard of reference, it is only from intercomparison that erratic behavior may be detected, or that confidence can be established. One cell conveys no information as to its constancy. An intercomparison of two cells would bring a variation of either to light, but would not disclose which cell varied. Therefore, three is the smallest group with which interchecks could have significance in detecting an erratic cell. Larger numbers of cells make for greater assurance, yet very large groups are unwieldy and expensive. Five or six cells make an excellent compromise. Several standardizing laboratories use three groups of three cells each, keeping one group as a stay-at-home reference, and alternately exchanging the other two groups for comparison with other standards groups, such as the NBS primary group.

The simplest mounting arrangement is an open rack

A - Copper cups
B - Rubber strip
C - Varnished tubing
D - ⅛" white wood
E - 20 oz. copper
F - ⅛" brass
G - Standard saturated cell.
H - Engravers wax
J - Thermometer tube
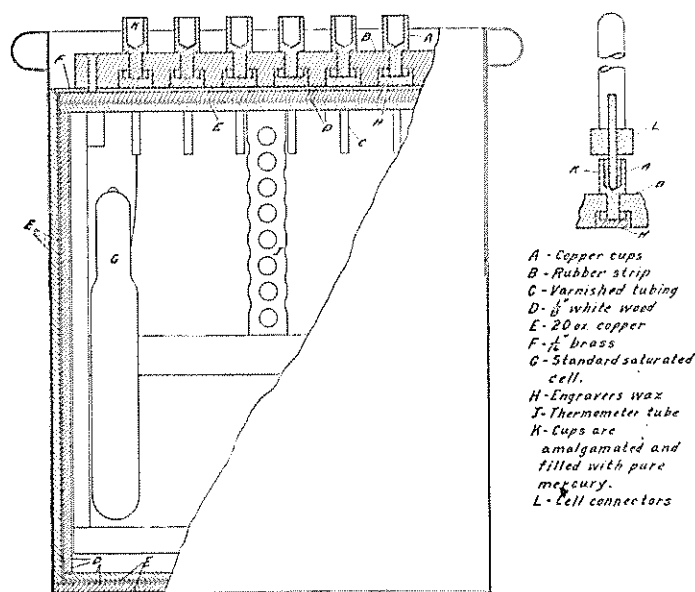K - Cups are amalgamated and filled with pure mercury.
L - Cell connectors

Fig. 1—Double-walled box and rack for six saturated standard cells. Cells remain at mean temperature of bath to 0.001°C if open bath regulating cycle is <8 minutes and < ±0.04°C.

upon which the cells rest, supported under the cross arms on felt pads, and with the electrodes hanging freely in the oil or air bath. Across the top are copper pins, to which the cell leads are connected on the bottom, with the external connections made on the top. In a constant temperature air bath, with the low heat transfer capacity of still air, such racks serve admirably. In oil thermostats, if there are any temperature gradients, the two electrodes of a cell may be at different temperatures. No difficulty is experienced from this cause in well-designed oil thermostats. If such trouble is experienced, the situation can be much improved by simply placing the rack in an open-topped metal container.

A more elaborate mount, with the cells completely enclosed in a double-walled metal box and with no metal connections between the walls of the boxes except the six pairs of small lead wires, is furnished with mercury cups arranged so that the connections may be changed under oil. Such elaborate mountings become necessary when reproducibility of intercomparisons within a few tenths of a microvolt is required (Fig. 1).

Unsaturated cells are mounted for laboratory use in bakelite or metal cases, provided with binding posts, pins, or plug-in connections for convenience in connecting. Most of the cells mounted in bakelite or plastic cases are also encased in a metal lining, usually copper, for equithermal shielding [19]. Immediately surrounding the cell is a layer of felt or other material acting as a mechanical cushion and a thermal insulation.

If standard cells are used within the cases of instruments, especially if heat-dissipating resistors or vacuum tubes are in the same case, every precaution should be taken to keep the operating temperature of the cell as little above the ambient as possible, since there will otherwise be a change in temperature associated with each operation of the instrument.

TESTING

The most important and most frequently made measurement on a standard cell is the determination of its EMF. Excepting the measurements in terms of cgs standards, such as the current balance, or of electrochemical equivalents, such as coulometers, practically all measurements of standard cell EMF are comparisons with other standard cells. Every type of potentiometer may be used, but the best methods are those which take advantage of the fact that intercomparisons of standard cell emfs are nearly one to one ratio measurements, and therefore can be made with very high over-all accuracy with relatively low accuracy measurement of the difference between the cell being measured and the cell being used as standard.

The standard cell potentiometer described by Eppley and Gray [20] utilizes this advantage, as do the direct difference measurement methods such as the Brooks comparator [21], the Weston model 1000 comparator [22], and the Eppley comparator [23]. In all these comparators, the cell used as reference standard is connected in opposition to the cell being measured, and the small difference in EMF is opposed by a measurable drop across a resistance. It readily can be seen that an accuracy of only one per cent in the measurement of the difference in EMF, if that difference is less than 10 μv, will result in a determination of the EMF of the cell under test to within 0.1 μv, or one part in ten million, in terms of the reference standard.

Although accuracy requirements are very easy to meet, the matter of thermal EMF's in the standard cell-galvanometer circuit are another matter. "Thermals" in the instrument and galvanometer circuit can be compensated by an opposing circuit, or cancelled by making two measurements with the polarity of the measured and measuring EMF's reversed with respect to the galvanometer. Neither of these methods, however, either detects or corrects for thermal EMF's in the circuit connecting to the cells. These must be reduced to a minimum, as by making the connections with mercury cups under oil in a thermostat (Fig. 2).

In the intercomparison of unsaturated cells, or the comparison of unsaturated cells with saturated standards, absolute accuracy of measurement beyond 0.001 per cent is not required, although in testing (*e.g.*, temperature coefficients) precision and reproducibility to 1 ppm is often required. If it is required to use an ordinary dial or dial and slidewire potentiometer for standard cell comparisons, and the calibration of the potentiometer is not known, the direct substitution method of measurement, albeit less convenient, is more accurate than the normal method, where the standard emf is introduced through a standard cell dial. How much more accurate depends upon the particular circuitry details of the potentiometer. In the direct substitution method, the standard of reference is connected to the EMF posts of the potentiometer, the dials set to the value of the
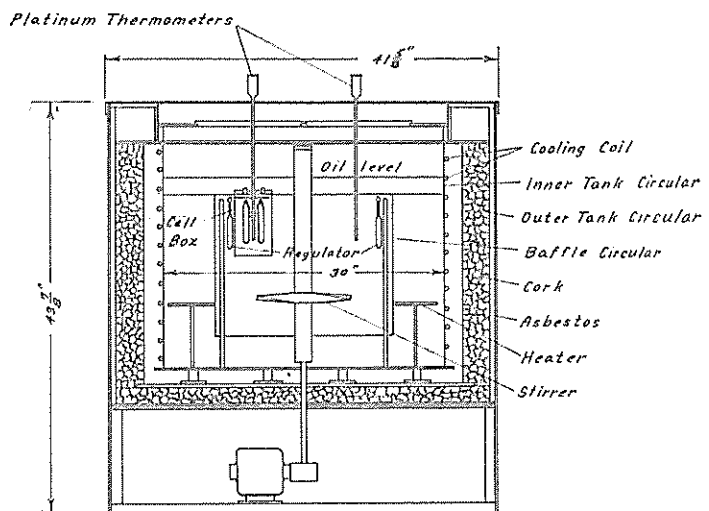

Fig. 2—Oil bath for six groups of six each, saturated standard cells. Oil required, 80 gallons. Heaters, 150 watts maximum. Stirrer, 80 rpm. Regulators, mercury-in-glass type, controlling heater through relays.

standard, and the galvanometer balanced with the current-adjusting rheostat. The cell under test is then substituted across the EMF posts, and the galvanometer balanced by adjusting the main dials or slidewire. As there will be little change in the dial or slidewire settings, the calibration errors of the instrument will be very nearly the same both in standardizing and in measuring the unknown, and therefore will cancel.

In highest precision measurements, the characteristics of the galvanometer may be the limiting factor. The internal resistance of the two cells connected in series-opposition in the difference method determines the external damping requirement for the galvanometer, which should usually be 800 to 1000 ohms. The precision of measurement sought determines the sensitivity requirement. In the Brooks and the Eppley comparators, where 0.1 μv is measurable, at least 5 mm deflection for 1 μv is required. In the Weston model 1000 comparator, 0.5 mm for 1 μv would be required to realize the instrument's 1-μv precision. An all copper electrical system in the galvanometer, and soldering the connections to the galvanometer, instead of using the binding posts, makes for less annoyance from disturbing thermal and contact EMF's, although errors from these sources can be compensated or corrected.

The tests for a standard cell must establish, within the limits expected for the type, that:

1) The EMF is correct.
2) The EMF is constant with respect to time.
3) The EMF is properly related to temperature.
4) The internal resistance is correct.

The first two conditions are simultaneously determined by a series of EMF measurements at normal room temperatures over a period of time. For the industrial types of unsaturated cells, in which 0.1 per cent accuracy is usually sufficient, this series could consist of a

minimum of three measurements taken one each at four, six, and eight weeks after assembly. For an unsaturated precision type cell to be certified to 0.01 per cent, ten measurements over a period of four months would be required.

If the electrolyte of a cell is of such $CdSO_4$ concentration that the temperature coefficient of EMF is minimal over room temperature ranges, the EMF would be 1.0191 volts [4]. However, the cell reaction (discussed above under types of cells) predicts, with the passage of time, a decrease in EMF and an increase in electrolyte concentration, therefore some manufacturers aim for a nominal EMF of 1.0192 to 1.0193 volts for new cells.

A newly assembled cell requires "aging" before coming to constant EMF. The electrolyte must become saturated with mercurous sulfate, at least in the cathode region, and a constant condition established between Hg_2^{++} and the cadmium amalgam. Often, in spite of careful washing, the mercurous sulfate retains traces of sulfuric acid, which must become distributed throughout the entire electrolyte. Details of technique can cause very wide variations in aging characteristics, but, in generalities, unsaturated cells are aged to constant EMF within 0.01 per cent in one month, and within 0.001 per cent in three months.

The third condition requires, for an unsaturated cell, that the temperature coefficient of EMF and the effect of a sudden temperature change be determined. A typical test would be to measure daily the EMF of a cell in an oil thermostat at a temperature slightly above room temperature (e.g., 28°C) until it is constant within 10 μv for three days, then quickly move the cell to another thermostat at a higher temperature (e.g., 33°C). The effect of the sudden change can be determined by a series of EMF measurements beginning immediately upon the transfer. Since this is an increase in temperature, the EMF aberration (hysteresis) will probably not persist more than a few minutes. Another series of daily measurements will establish the value at the higher temperature. From these observations the temperature coefficient for the interval selected may be calculated. In unsaturated cells over the 28°C–33°C interval, −1 to −5 $\mu v/°C$ are typical. If the cell is now returned quickly to the lower temperature thermostat, the effect of the sudden decrease in temperature may be observed. An aberration in EMF of 100 μv 24 hours after a change from 33°C to 28°C is too large to tolerate in a new cell. A good cell of modern design should be within 100 μv (0.01 per cent) within an hour of such a change. It is to be expected that hysteresis will increase, both in magnitude and duration, as the cell becomes older. This increase in hysteresis with time is most marked in cells containing little free acid and in cells containing untreated or incompletely treated cork washers [18].

An easier check on the hysteresis may be made by heating the cell to 40°C in an oven, allowing about 4 hours to be sure the cell is brought to temperature, then
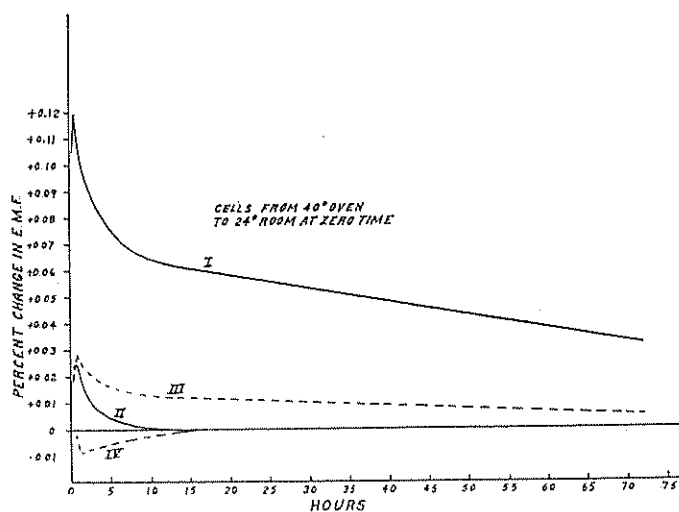

Fig. 3—Lag in reaching voltage equilibrium (hysteresis), unsaturated cells. Curve I, cork washer construction, four years old. Curve II, cork washers, new cell. Curve III, polystyrene plug construction, eight years old. Curve IV, polystyrene plugs, new.

removing the cell to room temperature (20°C–25°C) and observing the emf from time to time as it cools. A new cell should not be in error by 0.01 per cent 24 hours after such treatment. An old cell may require as much as a week to return to its normal EMF; however, such a cell will probably be in error most of the time due to the effect on it of the ambient temperature variations, and should not be trusted as a high quality standard (Fig. 3).

The fourth condition hardly needs testing, except in design work, as the internal resistance in a type of cell of particular dimensions and construction varies little from cell to cell. However, defects of manufacture such as entrapped air in the electrolyte path or broken internal leads can be detected by measuring the internal resistance, for which reason it is generally measured on every cell at the conclusion of the other tests. A 60-cycle bridge, such as the Leeds and Northrup No. 4960 is convenient and adequate. However, such a bridge does present a closed circuit to the cell, and therefore draws some current. If the measurement is made quickly, and it can be done in a few seconds, no permanent injury to the cell results. If it is desired to avoid discharging any current from the cell, this can be accomplished by using three cells and opposing them in pairs in series opposition and measuring the resistance of the pairs on the bridge. A set of three measurements permits calculation of all three individual resistances.

Since precise equipment to measure EMF is almost always at hand where standard cells are used, the following simple method for estimating the internal resistance of a cell is given:

1) Measure the EMF of the cell, E.
2) Connect a high resistance, R (e.g., 1 megohm) across the cell terminals.

3) Quickly measure the voltage drop, V, across the resistor.

4) Immediately disconnect the resistor.

Then the resistance of the cell, R_{sc}, will be

$$R_{sc} = \frac{E - V}{E} R,$$

or approximately, since E is within 2 per cent of unity,

$$R_{sc} = R(E - V).$$

This measurement is completely valid only if the total EMF of the cell, E, is the same under current drain as under no-load condition. However, this is not always the case. Many cells, and especially old cells, give strong evidence that the total EMF generated by the cell is less when a current is being withdrawn. The resistance as measured with an ac bridge is always less than that measured on a dc bridge. For new cells in good condition, the ratio is from very nearly unity to 1.7. Age, current withdrawal, and high temperature storage all increase the ratio. Table I lists the results of tests of

	DC Resistance			AC Resistance
	AC Resistance			sistance
	Average	Maximum	Minimum	Ohms
New, 25°C	1.2	1.3	1.1	352
After 1 year at 46.5°C	1.8	2.3	1.5	235
After 1 year at 55°C	6.3	7.4	4.7	196
After 1 year at 64°C	37.2	109.0	14.0	192

several groups of cells of the Eppley Cat. No. 100 type, unsaturated, precision laboratory standards of 350 Ω nominal resistance and 500 Ω guaranteed maximum resistance new and after one year continuously maintained at elevated temperatures. The resistances were measured at the storage temperatures, which accounts for the lower ac resistances at higher temperature. The ratios remained the same in further tests after the cells had cooled at 25°C.

A cell of the same type was discharged at 700 μa for 14 hours, in an oil thermostat at 28.16°C. Before the discharge the ratio dc/ac resistance was 370 ohms/342 ohms = 1.1. After discharge, it was 580 ohms/368 ohms = 1.6, five days later, 567 ohms/367 ohms = 1.5.

The ratio of the resistance as measured by a self-generated dc method to that as measured by an ac method is therefore a useful indicator of instability of EMF under small current drains [24]. It has been observed that increased hysteresis and general instability of EMF often appear simultaneously with increase of the apparent internal resistance as measured by the dc

method. The ac resistance increases only from gas bubbles in the electrolyte, separated electrode components, broken wires, etc. Therefore, the apparent increase in resistance as measured by the dc method can lead to a criterion for removing unstable cells from service. General Electric Company's West Lynn standards laboratory removes from precision service a cell of 100 ohms nominal maximum resistance (manufacturer's guarantee) when the apparent internal resistance by the dc method reaches about 300 ohms [25].

EFFECTS OF TEMPERATURE

Saturated Cells

Temperature is by far the most important environmental condition affecting standard cells in use.

Its effect has been the subject of several definitive investigations insofar as the saturated cell is concerned. Wolff [26] determined the relationship between emf and temperature over the range 0° to 40°C. The International temperature formula,

$$E_t = E_{20} - 0.0000406(t - 20) - 0.00000095(t - 20)^2 + 0.00000001(t - 20)^3,$$

based upon his work, is now generally accepted as describing the relationship with great accuracy over the commonly used temperature range. In this form, it corrects from the 20°C EMF of the cell, which was convenient when the assigned value of 1.0183 International volts at 20°C for the Normal cell was part of the basis of definition of the electrical standards. Now that 20°C has no greater significance than any other temperature, it would seem more desirable to use the equation referred either to its inflection point at 3°C, which leads to the most simple mathematical form, or to 0°C, in which case the operating temperature on the Celsius scale may be directly substituted in the equation.

Furthermore, since the equation is based upon the International volt, it is not strictly correct for any other unit. However, if its form is altered to:

$$E_t = E_{20}[1 - 0.0000399(t - 20) - 0.00000093(t - 20)^2 + 0.00000001(t - 20)^3]$$

and the appropriate calculations made to refer to other more convenient temperatures, the following equations result:

$$E_t = E_{3.1}[1 - 0.00000143(t - 3.1)^2 + 0.00000001(t - 3.1)^3]$$

$$E_t = E_0(1 + 0.0000093t - 0.00000306t^2 + 0.00000001t^3).$$

In all these expressions, we have a coefficient in the bracketed term, instead of an additive correction factor, and the equation remains correct regardless of the unit in which E is expressed.

However, for practical work, the formulas leading to additive corrections are easier to apply, therefore the International formula and the Vigoureaux and Watts [27] formula (discussed below) are here presented with the coefficients calculated to apply from 28°C:

$$\Delta e = -53.9(t - 28) - 0.71(t - 28)^2 + 0.01(t - 28)^3$$

(based on the International formula)

$$\Delta e = -52.88(t - 28) - 0.802(t - 28)^2$$
$$+ 0.0018(t - 28)^3 - 0.00015(t - 28)^4$$

(based on the Viroureux and Watts formula).

In both of these formulas, Δe is the difference in microvolts from the 28°C EMF of the cell, and t is the temperature in °C. These recalculations of the constants are suggested because 28°C has come into such general use as a maintenance temperature for standard cell groups. 28°C being above normal room temperature, thermostats can be operated at that point without cooling or with such simple cooling as a coil carrying tap water. Higher temperatures are undesirable because of the effect on the oil in the thermostat, because of the higher power required in the heater, and because of the possible acceleration of aging in the cells.

At the extremes of the operating range of primary standards, we must go to the work of Vigoureux and Watts [27] for the lowest temperatures, and of Vinal and Brickwedde [13] for understanding of the upper extreme.

The Vigoureux and Watts temperature formula is:

$$\Delta e = 39.39(t - 20) - 0.903(t - 20)^2 + 0.0066(t - 20)^3$$
$$- 1.5 \times 10^{-4}(t - 20)^4,$$

Δe being the difference in microvolts from the 20°C EMF of the cell. It describes the relationship at temperatures below 3°C better than the International formula. It does not, in our experience, conform to experimental data quite as well as the International formula at temperatures between 20°C and 35°C, although the differences never exceed 14 μv.

The work of Vinal and Brickwedde brings to light a transition in the $CdSO_4$-H_2O equilibrium at 43.4°C, which definitely sets the upper limit of temperature for present types of saturated standards. They found from both EMF and solubility curves that 3 $CdSO_4 \cdot 8$ H_2O is the stable form below the transition temperature, and $CdSO_4 \cdot H_2O$ above. However, each form may exist for long periods in the temperature range of stability for the other. This metastability leads to great uncertainty as to what the value of EMF would be for a cell that had been heated above the transition point. The fact that several workers, investigating the temperature-EMF relationship, have measured cells at temperatures above this point and found them to have EMF's that all on the curve of the International temperature formula, leads one to believe that, as suggested by Vinal and Brickwedde, the transition does not take place without some seeding of the monohydrate, or is so slow as to be insignificant when the transition temperature is exceeded by only a few degrees.

Combining the work of Wolff, Vigoureux and Watts, and Vinal and Brickwedde, we get the curve shown in Fig. 4 for the EMF vs temperature of a saturated cad-
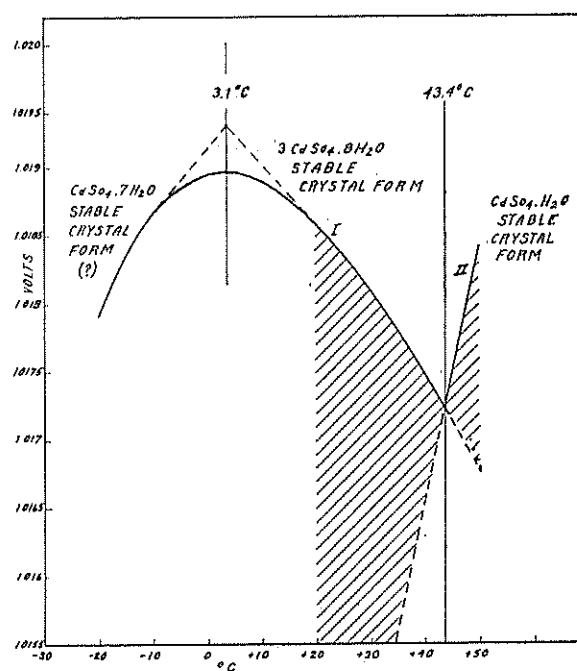

Fig. 4—EMF-temperature curve for a saturated cadmium standard cell, electrolyte 0.042 N H_2SO_4, calculated from Vigoureux and Watts formula. Above 0°C, average of values from International formula and Vigoureux and Watts formula. Straight line, $E_t = E_{43.4} + 0.000173$ $(t - 43.4°)$. Dotted portions intersecting at 3.1°C, hypothetical. Dotted portion intersecting at 43.4°C, observed.

mium standard cell at stable equilibrium at the given temperature. The question immediately arises whether the inflection of the curve at about 3°C, which has been observed repeatedly, might not also represent a crystal form transition, and whether some limitation as to the lower limit of temperature analogous to the upper limit situation described above, might not exist. If so, it would impose a limitation on the transportation of primary and highest grade secondary standards in winter time, and would indicate that for saturated cells to be used under conditions of highest accuracy, the 4°C to 40°C limits of temperature should be observed, not only as operating limits but also as the extremes to which the cells should ever be exposed.

Be that as it may, experience demonstrates that saturated standard cells have been exposed to temperatures in the range −8°C to 60°C for hours at least, if not for days or more, without damage to their accuracy as standards in terms of 0.001 per cent [28].

Regarding the operating temperature of saturated standard cells, 28°C, as indicated above, is the temperature of most general usage in the U.S.A. At the National Bureau of Standards in Washington, the comparisons of the national primary standards and most of the measurements for certifications of groups for use as secondary standards are made at 28°C. If we depart from the present practice of staying entirely within the temperature range wherein $CdSO_4 \cdot 8/3$ H_2O is the stable crystal, however, the inflection points of the temperature EMF curve may be desirable temperatures for maintaining standard cells if no greater disadvantage ap-