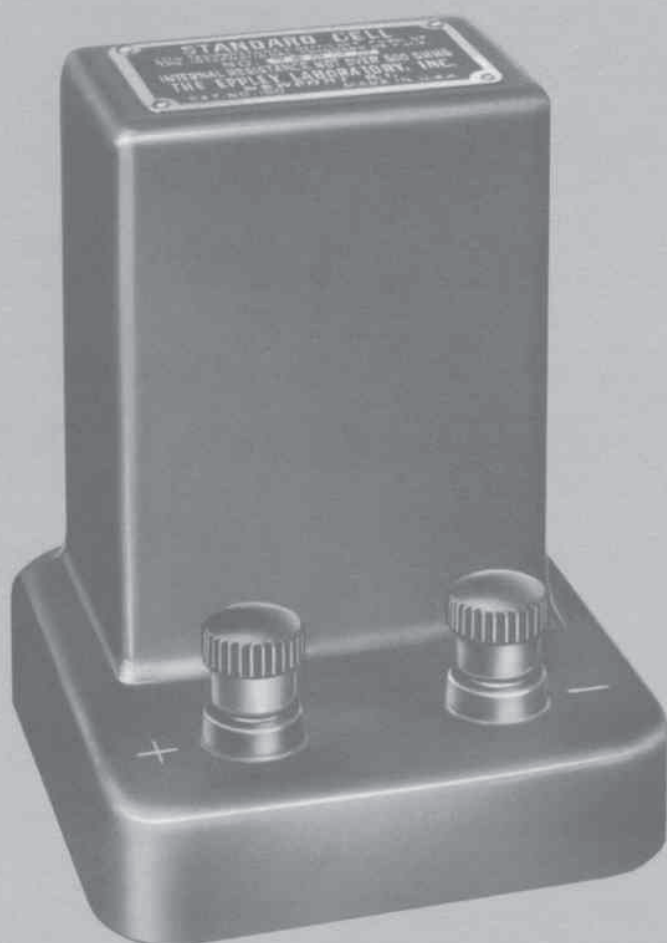


EPPLEY

BULLETIN NO. 1
NOVEMBER, 1968

STANDARD CELLS

*Precision
voltage references
for industrial and
laboratory use*



FPLAB

THE EPPLEY
LABORATORY, INC.

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*Scientific
Instruments*

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NEWPORT
Rhode Island

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THE ABSOLUTE SYSTEM OF UNITS

In the absolute system, the units of time, length and mass are fundamental, and all others including the electrical units of the ampere, ohm and volt are derived from them. Thus, electrical measurements are in agreement with measurements in other fields of science and engineering. This principle is most important theoretically; nevertheless, the most convenient means of realizing and maintaining the standards of electrical measurement still remain the standard cell and the wire resistor.

HISTORICAL

Jaeger, in the first chapter of his "Die Normalelemente und ihre Anwendung in der elektrischen Messtechnik", an early fundamental book, says: "The following conditions must be laid down for normal elements, regarding as such in the narrower sense only hydro-elements with metal electrodes:

- "(1) Their electromotive forces must remain constant under the same external conditions (of temperature) and
- "(2) Their electromotive forces must not be changed either by the withdrawal of current from the system, or by the passage of current through it, when the current does not exceed a certain fixed value for each type of cell, as well as that
- "(3) They must be reproducible."

VARIOUS SYSTEMS

The Daniell cell and the Fleming type of Daniell cell are among the systems that were

considered. These consist of a zinc electrode in a solution of zinc sulfate, in contact with a copper sulfate solution in which is a copper electrode. Both of the salts used are very soluble, diffusion is rapid and the zinc is rapidly attacked by the copper sulfate.

The Gouy cell is not reversible. When current is passed through it, mercurous sulfate is formed, upsetting the equilibrium.

The De La Rue, Helmholtz, and Hibbert cells all have a mutual disadvantage, containing, as they do, zinc chloride which is a very poorly defined substance chemically.

Finally considered were the Clark and Clark-Carhart cells, and the two Weston cells. The Clark cell consists of zinc amalgam, a saturated solution of zinc sulfate with an excess of crystals, mercurous sulfate, and mercury; the Clark-Carhart consists of the same system without an excess of zinc sulfate. The first is reproducible to a satisfactory degree and both are constant. However, the Clark cell has a high temperature coefficient, about 0.00119 volt per degree Centigrade; and that of the Clark-Carhart is about 0.00053 volt per degree Centigrade. These are not deciding disadvantages as temperatures may be controlled, but there is a tendency for the glass containing-vessels to break due to expansion of the sealed-in platinum wires because the platinum forms an alloy with the zinc, and also, gas often forms over the electrodes, open-circuiting the cell. Freedom from these troubles, together with a lower temperature coefficient, brought the cadmium cell ready acceptance. When properly made the cadmium cell has a very high degree of constancy and in addition a lower temperature coefficient than the corresponding type of zinc cell.

From the above discussion it will be seen that the last two systems described are the ones that most nearly approach the conditions laid down by Jaeger. The normal or saturated cadmium standard, also called the normal Weston

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cell, is the one on which the Bureau of Standards has based its standard for the volt since 1911. It consists of the combination:

Hg — Hg₂SO₄ — saturated CdSO₄ solution with excess of solid CdSO₄ — Cd amalgam.

THE SATURATED CELL

The container of the saturated cell is an H-shaped glass vessel with sealed-in platinum wires at the lower ends of the vertical legs for electrical connection. In one leg there is mercury and in the other, cadmium amalgam. The mercury electrode is covered with a mixture of mercurous sulfate and finely ground cadmium sulfate crystals. A layer of larger cadmium sulfate crystals is placed upon the surface of both the amalgam and the mercurous sulfate. The cell is filled to above its crossarm with a saturated solution of cadmium sulfate after which the open ends of the H-tube are sealed by fusing in a flame to insure air-tightness. Mercurous sulfate is slightly light-sensitive and exposure of cells to light should be limited to short, infrequent periods.

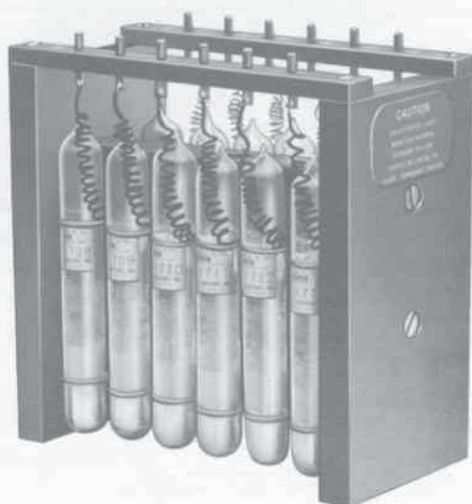


Figure 1.
Bank of six saturated cells (large)
(Cat. No. 101G6)

TYPES OF SATURATED CELLS

The Eppley Laboratory produces both the non-shippable (Cat. No. 101) and shippable (Cat. No. 114) types of saturated cells. The Cat. No. 101 is a relatively large, H-shaped cell (4 3/4" x 2 1/2" x 5/8") which has been employed by laboratories throughout the world in establishing a primary reference volt. Cells of this type must be hand-carried when it is desired to transport them, as damage will occur to the cells if they are not maintained in an upright position.

The Cat. No. 114 miniature shippable saturated cell (3 3/4" x 1" x 3/8") provides a reliable voltage reference, accurate to 0.001%, which combines the high stability and long life of a saturated cell with the portability that is a feature of unsaturated cells. Shippability is accomplished through utilization of a patented linen covered plastic septum to retain the electrode materials in place. This type of septum has been used for over ten years in the construction of portable standard cells, permitting them to be shipped without detrimental effects.

EFFECTS OF TEMPERATURE

Temperature is by far the most important environmental condition affecting standard cells in use. Based on the work of Wolff* the international formula:

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

has been accepted as most accurately repre-

*Wolff, Bur. Stan. Bull. 5, 326 (1908)

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senting the relationship of the emf of a saturated cadmium cell to temperature between 0° and 40°C. This amounts to approximately $-40 \mu\text{V}/^\circ\text{C}$ at 20°C.

Because 28°C is extensively used as a maintenance temperature of standard cell groups, a more practical form of the international formula with coefficients calculated to apply from 28°C is:

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

In this formula Δe is the difference in microvolts from the 28°C emf of the cell, and t is the temperature in °C.

As a slow transition occurs in the form of the cadmium sulfate crystal at approximately 43°C with an associated change in emf, 40°C is recommended as the safe upper limit to which saturated cells should be exposed, while -15°C is recommended as the lower limit to prevent freezing of the electrolyte.

Since saturated cells accommodate themselves rather slowly to changes of temperature, they should be maintained in an environment controlled to $\pm 0.01^\circ\text{C}$, or better, for from 36 hours to one week before measurements are commenced, and also during the time measurements are being made, if a constancy within ± 5 microvolts is to be secured. To attain maximum stability (1 to 2 μV), a waiting period of 4 to 6 weeks may be necessary.

Because of its large temperature coefficient, the saturated type of cadmium cell is not convenient for use as a general laboratory standard unless a primary standard comparable to the National Bureau of Standards is desired. A mounted unsaturated cell such as the Eppley Cat. No. 100, accurate to 0.005%, is recommended as a general laboratory standard. For those who do desire a primary standard, we regularly list Eppley saturated cadmium cells in groups of three to six, mounted on a bakelite rack. We do not list fewer than three because a smaller number will hardly give the results

desired or attainable with saturated cells. With only one reference standard, there is no possibility of checking its constancy if it should be disturbed by either an internal or an external cause. Two standards may be used to check each other, but if a variation should be evident, it would be impossible to determine where the variation lay. This leaves three as the smallest possible number which could be used to obtain fairly reliable results on the group. It is evident that the greater the number of standards, the greater the significance that may be attached to the results obtained.

We, as well as customers whom we have supplied with Eppley saturated cadmium cells, have found that groups of six satisfy the requirements for the maintenance of a voltage standard.

The cells of such groups may be intercompared, providing a very reliable check of the group and showing the performance of the individual cells. The method of making the intercomparison is to use each cell in turn as the standard and against it measure each of the remaining cells in the group.

CERTIFICATION

An Eppley certificate stating the value of the emf to 0.0001% is generally provided with all saturated cells. A National Bureau of Standards "Report of Calibration" can be obtained instead, if required, in which case an additional charge is involved.

CONSTANT TEMPERATURE BATHS

The Eppley Laboratory manufactures both oil and air baths suitable for maintaining satu-

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rated standard cells at temperatures controlled to 0.01°C or better. Selection usually depends on the cell capacity desired as well as convenience in operating and handling.

The Model 105 oil bath has been designed for the maintenance of saturated cells as a primary standard, and is similar to equipment used in the various national laboratories for the establishment of the volt. It has a capacity of 36 cells in groups of 3 or 6. A smaller oil bath (Model 200) with a capacity twelve cells can also be supplied which will provide a voltage reference with a part per million stability.

Several models of constant temperature air baths are available. Model 106, described in Bulletin 12, has a capacity of six saturated cells of the 101 type, and has proven an excellent unit for maintaining a primary voltage reference. Model 121 has been developed as a standard voltage reference employing Eppley miniature saturated cells of the Cat. No. 114 type. Literature describing these and other air baths, including models designed for rack mounting, is available on request.

MEASURING INSTRUMENTS

The Eppley Standard Cell Comparator (Cat. No. 107) described in Bulletin 11 has been designed especially to provide an instrument for accurately comparing, to tenths of a microvolt, the difference between the electromotive forces of two standard cells connected in opposition. In addition, a high sensitivity galvanometer and a microammeter are necessary to obtain the measurements.

The Eppley Standard Cell Potentiometer (see Bulletin No. 7) is a precision instrument designed especially for the rapid and accurate measurement of unsaturated standard cell voltages, particularly where routine measurements must be made in quantity.

THE UNSATURATED CELL

For a high-accuracy secondary standard the Eppley Cat. No. 100 unsaturated cadmium standard cell has been generally accepted. This type of cell is similar in form to the normal cell except that the solution of cadmium sulfate is unsaturated at ordinary room temperatures, no excess of the solid cadmium sulfate being added to either the mercurous sulfate or the solution. The container of the unsaturated cell is also an H-shaped glass vessel. This laboratory uses septa to hold the electrodes and "depolarizer" in place, making the cell readily portable.

TEMPERATURE COEFFICIENT

The temperature coefficient of a cell is the algebraic sum of the temperature coefficients of the two electrodes, the electromotive forces of which are of opposite sign; that of the mercurous sulfate or positive limb being positive, and that of the cadmium amalgam limb being negative. Therefore, it is important that both electrodes be held at the same temperature.

The principal advantage of the unsaturated cell is its small net temperature coefficient which averages only $-3 \mu\text{V}/^{\circ}\text{C}$ between 4°C and 40°C . (See Figure 2.)

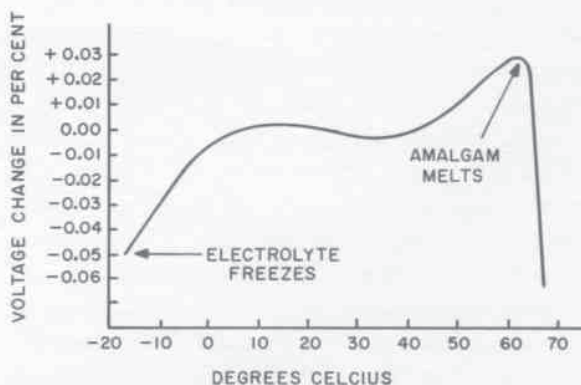


Figure 2.