HYSTERESIS IN STANDARD CELLS

Hysteresis, although definable as the erratic behavior of the voltage while the cell is coming to equilibrium following a change of temperature, is very difficult to express in figures, no satisfactory unit or standard having been devised for it. From one standpoint it may be considered as the length of time necessary for the establishment of an electromotive force of accepted value for the new temperature, following a temperature change. From another standpoint it may be considered as the magnitude of the variation from the normal value of the cell after a sufficient time has been allowed for it to come to some temperature differing from that at which it was previously maintained, or these two factors may be combined.

The extent of hysteresis is related to cell size, internal construction and age. Eppley miniature type cells have always exhibited very low hysteresis. Through an improvement several years ago in the construction of our other unsaturated cells, objectionable hysteresis frequently observed in older cells has been essentially eliminated. For several years prior to incorporating this manufacturing change in our production, cells so built underwent a rigorous test program which showed that they had greatly improved performance not only with regard to hysteresis but also with regard to the effects of aging and, to a lesser extent, temperature coefficient. Typical hysteresis for Eppley unsaturated cells following a 15°C drop in temperature is a 0.02% voltage change which returns to within 0.005% of the stable value in 2 hours. As hysteresis is smaller with an increase in temperature, an equivalent rise of 15°C produces a negligible effect. (Manufacture of the improved cells began with the following serial numbers: Cat. No. PYR, 755269; Cat. No. 100, 775880; Cat. No. 103, B5658.)

In order to secure the best performance from unsaturated cells, they should be placed where they are to be used and allowed to stand for 24 hours before measurements are made. This location should be free from drafts and localized hot or cold zones such as may be occasioned by the proximity of a radiator, steam pipes, rheostats carrying heavy currents, electric lamps, or windows allowing the rays of the sun to reach the cell case. As an aid to minimizing the harmful effects of such temperature inequalities our Catalog Numbers 100 and 103 unsaturated standard cells are contained in a molded bakelite case which is lined with an equithermal shield of metal that assists in the equal distribution of temperature around the cell.

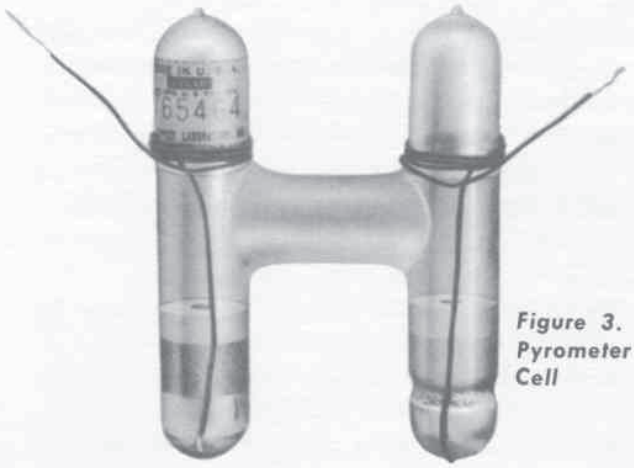

Figure 3. Pyrometer Cell

In addition to the precautions given above, cells should not be operated at temperatures below 4°C nor above 40°C. Experiments with cells taken beyond these limits show the extreme upper limit of reliability to be in the vicinity of 50°C. It is, therefore, recommended that for precision work this limit be not too closely approached. At about 4°C the solution of an unsaturated cell is presumed to reach a state of saturation, the concentration being so calculated. Hence when this temperature is reached, the cell assumes a temperature coefficient corresponding to that of the normal or saturated cell.

When all necessary precautions are taken, the Cat. No. 100 standard cell is capable of 30 day stability of the order of ±0.001%.

STANDARD CELLS

ACCURACY AND STABILITY

In the past the accuracy of emf stated for Eppley unsaturated cells, of both the mounted and unmounted types, has indicated the limits in emf that could develop over an extended period of time and over a temperature range, usually 4-40°C (40-104°F) rather than the narrow emf limits of a new cell at a stated temperature which is the result of careful control in the manufacturing process. Although past emf specifications of accuracy included stability, future accuracy specifications will list the emf values of new cells at 25°C in terms of our primary standards.

Certificates, however, will continue to state the voltage accuracy of mounted cells over a temperature range and time limit, taking into account the temperature coefficient and aging of the cells.

Stability or constancy is that property of a cell which enables it to maintain its initial emf. Operational conditions such as temperature change and current drain affect the short term stability of standard cells, while the long term stability is primarily affected by aging, operating temperature and use.

The constancy of the electromotive force of these cells is extremely satisfactory when correctly made, only a slight decrease in emf per year of about 15 microvolts for the Cat. No. 100 and 45 microvolts for the miniature type. This is attributed to a gradual replacement of the cadmium in the amalgam by mercury because of the diffusion of mercurous-ion, the cadmium going into the solution, increasing its concentration and decreasing the electromotive force of the system.

Use, with its attendant slight current drain while balancing the circuit, hastens this action and the above figure may more than double. In consideration of this it is recommended that the cells be recertified by the maker, or a laboratory equipped to render this service, once every year or two if an accuracy of 0.01% is desirable over this period. Cat. Nos. 100 and 103 cells, which have a guaranteed accuracy of 0.005%, should be recertified at intervals not exceeding one year.

STORAGE

It is recommended that standard cells be stored upright, in a dry place, at normal room temperatures, or slightly below. High temperatures are to be avoided, as the conditions contributing to the failure of old cells appear sooner in cells which are maintained at high temperatures. Figure 4 shows the accelerated rate of decrease of emf in unsaturated cells at high temperatures.

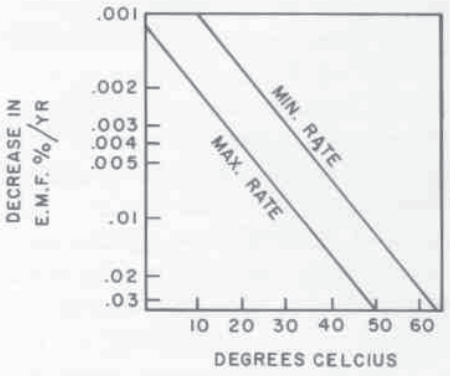

Figure 4.

ABNORMAL TEMPERATURES

During shipment and storage cells may be subjected to extreme temperatures of from several hours to several weeks duration. Time necessary for the cell emf to recover to within 0.005% of that at 25°C is given below for temperatures between −20 and +60°C.

Temperature	Recovery Time
+60°C	6 hrs
+40°	2 hrs
0	4 hrs
−10°	6 hrs
−20° (partial freezing)	4 days

At lower temperatures (below −30°C) breakage of the cell is almost inevitable. In view of the accelerated aging effect from high temperatures and the slow recovery rate from low temperatures, it is recommended that unsaturated cells be stored at temperatures between −10°C and +40°C.

CURRENT WITHDRAWAL

Extensive tests have been conducted in this laboratory regarding the amount of current that may be drawn from a standard cell without its voltage being affected. We have also investigated the magnitude of the change in voltage while undergoing a given current drain. From the results of these tests we can but emphasize that the cadmium standard cell is a standard of electromotive force for use in a potentiometer circuit and is not capable of supplying current to any marked extent without such use being detrimental to its primary purpose.

Current of the order of 100 μa may be drawn for a period of six minutes without permanently affecting cells, while time to recover to within 0.005% is less than 20 minutes for cells subjected to a current drain of 100 μa for 2 minutes. It is emphasized that to attain the best performance from any cadmium cell the current withdrawn should be as small as possible and not exceed 0.0001 ampere for more than a few minutes.

Based on results of over four years of continuous current drain tests, it may be stated that although the relationship between change in voltage and time is not a linear one, the decrease in emf per unit area of electrode produced by the withdrawal of small currents (up to 10 μa) is approximately 11 μv/coulomb cm^{-2}. Electrode areas of Eppley unsaturated cells are: Cat. No. 103, 5.5 cm^2; Cat. No. 100 and Cat. No. PYR, 1.43 cm^2; and all MIN cells 0.5 cm^2. In addition to the slow permanent change in emf of a cell resulting from current drain, the voltage will be immediately reduced by the magnitude of the IR drop upon closing the circuit.

Short-circuit tests show that a cell short-circuited for one-half hour took eleven hours to recover to within 0.07% of its original value and 36 days to come back to within 0.007%. Other cells short-circuited for one minute recovered to within 0.005% of their original values in less than four hours, while recovery from a ten second short-circuit required only ten minutes.

A voltmeter should not be used in an attempt to determine the voltage of a standard cell. The current drain caused by the ordinary voltmeter will be detrimental to the cell. For obvious additional reasons the reading will be entirely meaningless. Standard cell determinations should always be made by a null point method.

SHOCK AND VIBRATION

Eppley portable standard cells can withstand shocks of 50 g without damage to internal components or change in emf. In addition, they will pass the test for vibration as set forth in MIL-STD-202A, Method 201A. For low noise in fast response circuitry, special features (U.S. Pat. No. 2816946) have been incorporated in the MIN I cell. Because of their size and weight, type 103 cells are the most sensitive to mechanical shock. Nevertheless, they have been shipped successfully for many years.

OPERATING POSITION

Cells will remain operative when displaced up to 60° in any direction from the normal, upright position. Special miniature models (MIN I-H) can operate 90° from upright, or, as a

STANDARD CELLS

pair mounted together (MIN II), in all positions.

Although cells should not be stored in an inverted position, this condition might occur during shipment. Test cells inverted for as long as four days recovered immediately to within 0.005% after being restored to an upright position.

MINIATURE TYPE CELLS

The Eppley miniature type unsaturated standard cell is a small, light-weight cell of high accuracy and long life. Properly mounted, it is a reliable standard of emf, capable of 30 day stability of the order of ±0.001%.

Features covered by U. S. Patents and improvements in design have made the miniature cell practically hysteresis free, even at ages above five years. Because of its smaller size and weight, it responds more quickly to temperature changes than the other types of unsaturated cells. For example, after a 15°C drop in temperature, this cell recovers to within 0.005% of its initial value in less than 1 hour.

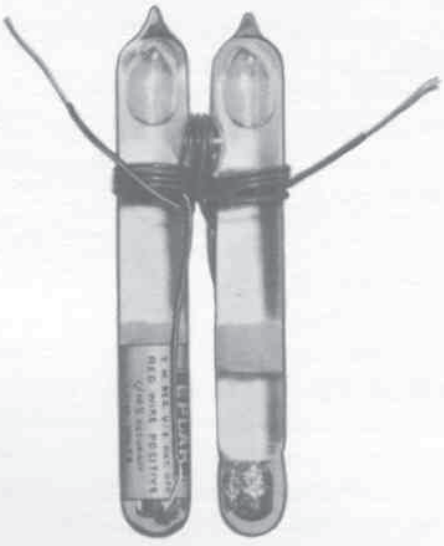

Figure 5.
Miniature Cell, Unmounted
(Cat. No. MIN. I)

Figure 6.
Miniature Cell, Mounted
(Cat. No. MIN. III)

For smaller temperature changes (5°C) recovery time is less than 10 minutes. However, this MIN type cell has the highest internal resistance of the unsaturated cells, and, because of its small electrode area, current drains have a greater effect on it than the other types. Nevertheless, this cell exhibits excellent recovery after being subjected to small current drains of short duration. In terms of 0.005%, the recovery time is approximately 1 minute for every 5 μa minutes of electrical discharge, while cells short-circuited for 10 sec. recovered to within 0.005% in 15 minutes.

SPECIAL MODELS

Special models of the miniature cell have been developed to meet unusual operating conditions. A ruggedized model (MIN I-R) has been designed to withstand extreme mechanical shock, while another model (Cat. No. 116) consisting of a cell encapsulated in a suitable epoxy resin has been developed to provide a sealed unit in the event of breakage of the glass H-tube.

We welcome the opportunity to discuss applications of cadmium standard cells where unusual environmental conditions must be tolerated.

RECERTIFICATION SERVICE

As a laboratory engaged in cadmium standard cell manufacture and research for over fifty years, we have available a complete facility for the testing and/or recertification of both saturated and unsaturated cells. Beginning with our reference standard, our facility includes the precision measuring instruments and experienced personnel necessary to adequately perform this service.

The primary reference volt consists of some 36 saturated cells ranging in age from 3 to 30 years which are maintained at a constant temperature in oil baths at 28°C. These cells are checked periodically (six cells every six months) at the National Bureau of Standards, Washington. The precision measuring instruments used are of our own design and construction and have given many years of reliable service. In addition, the trained personnel engaged in the recertification of cells have, on the average, 25 years experience.

The recertification of saturated cells requires from four to six weeks and can be accomplished either in our oil baths at 28°C or in the customers oil or air bath. After allowing a period of time for the cells to stabilize, a minimum of ten comparisons between the standard and test cell are obtained using the difference method. Based on these readings, a certificate stating the cell value to the nearest microvolt is issued.

Mounted unsaturated cells sent to us for recertification are handled according to whether they are of Eppley manufacture or of another make. Briefly, cells of Eppley manufacture are read upon receipt and the reading checked against our record file. The cell is then removed from the mount and inspected. If in satisfactory condition, the cell is remounted, allowed to stabilize for at least 24 hours, and given a series of readings necessary for certification. If the cell is damaged or for any other reason does not qualify for recertification, a report is sent to the customer stating that a new element is required to provide a certifiable cell. Upon authorization a new cell of the same type is mounted in the customer's case, a new name plate corresponding to the serial number of the replacement cell attached, and the repaired unit recertified. For cells of other than Eppley manufacture, the inspection and repair steps in the above procedure must for obvious reasons be eliminated. Otherwise the procedure is the same. If emf readings are satisfactory, a certificate is issued; if not, a report is prepared stating the reason or reasons the cell failed to qualify for certification.

In the case of unmounted, unsaturated cells for which certificates are not issued, the cell is given a visual examination, an emf reading and is tagged with its emf. A report is made if necessary. No charge is made for this service.

Readings on all unsaturated cells are obtained using a precision potentiometer especially designed for measuring standard cell emfs. A saturated cell is employed as the standard. Approximately three weeks is required to complete the testing and recertification of unsaturated cells.

All Eppley certificates show traceability to NBS, Washington, through the NBS test number of our reference cells. Values of unsaturated cells are stated to 0.00001 v.

STANDARD CELL LIFE

When maintained at normal laboratory temperatures and operative conditions, the usable life of reliable unsaturated standard cells is from five to ten years.

SPECIFICATIONS FOR UNSATURATED CELLS

UNMOUNTED

CATALOG NUMBER	TYPE	NOMINAL SIZE H W T	WEIGHT	RESISTANCE AT 25°C (OHMS, MAX.)	ELECTROMOTIVE FORCE AT 25°C (VOLTS)	RECOMMENDED USE
PYR	Industrial	3⅛x2⅜x¾	3 oz.	500	1.0193 ±0.0002	Potentiometric Recorders
100a	Precision	3⅝x2⅜x¾	4 oz.	500	1.0193 ±0.0002	Portable Potentiometers
103b	Low Internal Resistance	3⅞x2⅝x1	8 oz.	100	1.0193 ±0.0002	Deflection Potentiometers
MIN I	Miniature	3⅛x1x⅜	1¼ oz.	1200	1.0193 ±0.0002	Recorders & Digital Voltmeters
MIN I-H	Miniature	2⅝x1x⅜	1¼ oz.	1200	1.0193 ±0.0002	Horizontal Operation

MOUNTED

100	Precision	5⅛x4⅛x4⅛	1 lb. 5 oz.	500	1.0193 ±0.0002 Accuracy Certified 0.005%	Laboratory Standard
102	Students'	5¼x3⅛x1⅜	10 oz.	500	1.0186 ±0.0005 Not certified	Demonstration Standard
102R	Students' with 10,000 Ω series resistor	5¼x3⅛x1⅜	10 oz.	11,000	1.0186 ±0.0005 Not certified	Demonstration Standard
103	Low Internal Resistance	5⅛x4⅛x4⅛	1 lb. 10 oz.	100	1.0193 ±0.0002 Accuracy Certified 0.01%	Lab. Standard of Low internal resistance
*MIN II	Miniature	4⅝x1⁵⁄₁₆x1⁵⁄₁₆	6 oz.	1200	1.0193 ±0.0002 Not certified	All position operation
*MIN III-05	Miniature	4⅝x1⁵⁄₁₆x1⁵⁄₁₆	5 oz.	1200	1.0193 ±0.0002 Not certified	Instrument Internal Standard
MIN III-01	Miniature	4⅝x1⁵⁄₁₆x1⁵⁄₁₆	5 oz.	1200	1.0193 ±0.0002 Accuracy Certified 0.01%	Instrument Internal Standard
110	Miniature (10 Cells)	5½x5x3¾	3 lb.	10,000	1.0193 to 10.193 Accuracy Certified 0.005%	1 to 10 volt Standard

*Although not certified, the emf of these cells is guaranteed within 0.05% over the temperature range 4-40°C (40-104°F) All mounted cells are stocked with binding post terminals. Other terminals available on order.

The emf of unmounted cells is guaranteed within 0.1% between 4 and 40°C (40-104°F) provided the cell has been allowed to remain for a reasonable length of time at any selected temperature within this range.

SPECIFICATIONS FOR SATURATED CELLS

UNMOUNTED

CATALOG NUMBER	TYPE	NOMINAL SIZE H W T	WEIGHT	RESISTANCE at 25°C (OHMS, MAX.)	ELECTROMOTIVE FORCE at 28°C	RECOMMENDED USE
101	Non-shippable	4¾x2½x⅝	5 oz.	1000	1.018220 ±20μv Certified to 1μv	Primary Standard
114	Miniature Shippable	3¾x1x⅜	1½ oz.	1500	1.018220 ±20μv Certified to 1μv	Travelling Standard
325	SHIPPABLE	2½x2x⅝	2 oz.	1000	1.018220 ±20μv Certified to 1μv	Travelling Standard

MOUNTED

As saturated cells are usually sold in groups of three to six, it is convenient to have them mounted on a suitable rack for ease in transporting and handling. The Eppley Laboratory provides a rack with copper pin terminals for a mounted group of cells. In this instance ordering information should include the number of cells in the group as well as the type of cell desired. For example, six mounted cells of the Cat. No. 101 type would be identified as a 101G6. Groups of Cat. No. 114 cells can be similarly mounted.

Special mercury cup racks in thermally lagged containers for use in oil baths are available, and will be quoted on request.

All Eppley saturated standard cells are obtainable with National Bureau of Standards calibration reports. This entails an additional charge plus, in the case of non-shippable cells a messenger service charge of $150.00 for transportation to Washington, D. C. The resulting total price is F.O.B. Washington D. C. where pick-up of the cells must be made by the customer.