

pears to offset the advantage of zero temperature coefficient. The lower temperature inflection point at about 3°C in particular is very attractive in these days of mass produced mechanical refrigeration. Unfortunately, to date, there has been no report of any long duration test to assure us that there is no unknown, slowly appearing deleterious effect in the perpetual maintenance of a standard at 3°C. It is hoped that reports on such a test will be available from the research program of The Eppley Laboratory, Inc.

Vinal and Brickwedde have discussed the possibility of a check on the stability of primary standards by maintaining some cells with an all 8/3 hydrate crystal system and others with an all monohydrate system, expecting an exact one-to-one relationship of emfs at the transition temperature [13].

The 43.4°C transition temperature also merits consideration as an operating temperature for cells which may have to sustain nonoperating temperatures above that point from time to time, as the point on the temperature emf curve to which any cell, regardless of temperature history, should return. If one does not know at what temperature the cell has been in its more or less immediate past, one does not know where, in the hatched area of Fig. 4, its EMF at any particular temperature may lie.

Whatever operating temperature is chosen for a group of saturated cells, the temperature changes should be kept as small as possible, to avoid the solution and recrystallization of cadmium sulfate which accompanies a temperature change cycle. There is always the possibility that the recrystallizing cadmium sulfate will be deposited in interstices in the existing crystal mass in such a way as to increase greatly the internal resistance of the cell.

This effect causes most of the permanent damage to cells that have been accidentally overheated through thermoregulator failure.

#### Unsaturated Cells

Passing from the saturated standard cell, as a primary or very high accuracy secondary standard, to the ordinary high-accuracy secondary standard, brings us to consideration of the unsaturated standard cell. First, however, it should be mentioned that the saturated cell is much used in Europe as a working laboratory standard, usually in a thermally-lagged case, at room temperature. A thermometer is inserted into the case, and the value of the cell for the particular observed temperature is calculated or, more conveniently, read from a table. American usage strongly favors the unsaturated cell, with a negligible temperature coefficient, in terms of 0.01 per cent accuracy, over the range 4°C–40°C. Fig. 5 illustrates the typical EMF-temperature relationship for an unsaturated cell. It has not been as thoroughly studied as the saturated cell, and the inflection points are not well defined. However, one is inclined to suspect that a precise determination might show that they oc-

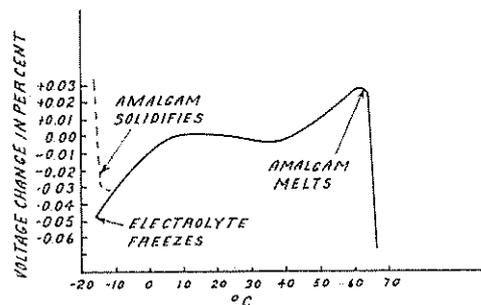


Fig. 5—Typical EMF-temperature curve for an unsaturated cadmium standard cell. Dotted portion, amalgam becomes single phase (solid) above freezing point of electrolyte.

cur at the same temperatures as the corresponding points on the saturated cell curve.

Since we do not now have any concern with the hydration of  $\text{CdSO}_4$  crystals, the solution being unsaturated at all temperatures except, possibly, between 3°C and 4°C, we are no longer limited by crystal transition. The limits of temperature imposed by characteristics of the cadmium amalgam must now be considered.

The behavior of cadmium amalgam with respect to EMF and temperature was determined by Smith [29]. He found that the EMF of a cadmium amalgam electrode in an aqueous cadmium sulfate solution is virtually independent of constitution of the amalgam as long as there are two phases present in the amalgam. The temperature span over which two phases can exist together is somewhat less than 50°C, and the temperatures of the limits of the span depend upon the composition of the amalgam. This would lead to the gloomy prediction that the limiting operating temperatures for unsaturated cells would be hardly more widely separated than those for saturated cells, were it not for one saving characteristic of cadmium amalgams.

This characteristic is the segregation of amalgam, when cooling slowly, into an inner cadmium-rich core surrounded by an outer, relatively mercury-rich layer. Therefore, on cooling a cell containing cadmium amalgam, there is a two-phase amalgam at the metal-solution interface at temperatures much below the point of complete solidification for an homogeneous amalgam of the same mercury and cadmium content. As a result, an amalgam of 12½ per cent cadmium content, which, if homogeneous, would become a single-phase amalgam (solid) at about 12°C, can be used, provided it was properly slowly cooled when first introduced, down to the freezing point of the electrolyte, which is below -17°C. The upper limit of use, at which the amalgam becomes entirely liquid, is about 65°C for a 12½ per cent amalgam, and about 51°C for a 10 per cent amalgam. If high temperature operation is desired, the amalgam may be further enriched to perhaps 15 per cent, which will remain a two-phase mixture to above 70°C. However, in the richer amalgams there seems to be less extension of range on the low temperature end from segregation in cooling; thus a 15 per cent amalgam might well be troublesome at temperatures below 20°C.

Manufacturers of standard cells usually use either 12½ per cent or 10 per cent amalgams. Often the saturated cells, intended for use over a more restricted temperature range, have 10 per cent amalgam which has characteristics coinciding well with that range. Unsaturated cells, on the other hand, frequently have richer amalgams, partly because of the greater need for reliable higher-temperature operation, and partly because the normal reaction of the cell tends both to decrease the cadmium content and to increase the mercury content of the amalgam.

When the complete solidification of the amalgam does not establish the lower limit of operation of a cell, the solidification of the electrolyte at a little below  $-17^{\circ}\text{C}$  does. Supercooling sometimes allows cells to remain operative to as low as  $-21^{\circ}\text{C}$ , but of course this should not be relied upon.

Fig. 6 illustrates typical behavior of an unsaturated cell at low temperatures.

Recovery of EMF towards original value is within 0.1 per cent almost the instant the electrolyte becomes liquid; within 0.01 per cent in less than an hour.

No permanent effects have been observed after freezing down to about  $-40^{\circ}\text{C}$ . At about this temperature, frequent breakage of the glass vessel has been observed, sometimes in the cooling cycle, and sometimes in warming back to operating temperatures. Breakage is not reduced significantly by slowing the cooling or rewarming. A pretty hypothesis based upon the known fact that mercury freezes at  $-40^{\circ}\text{C}$  was discarded when the same effect was observed in a sealed glass tube containing only cadmium sulfate solution, such as is used for the electrolyte in cells. Visual observation of those tubes disclosed that there is a change in the appearance of the frozen electrolyte near  $-40^{\circ}\text{C}$ , which indicates a transformation or transition accompanied by a volume change. Regardless of the explanation, the fact remains that breakage of the glass tube has been frequently observed only at temperatures near  $-40^{\circ}\text{C}$ , leading to the statement that standard cells should never be exposed to temperatures as low as  $-40^{\circ}\text{C}$ .

To fix the upper limit of nonoperating temperature requires consideration of duration of the high temperature. Good, modern, unsaturated standard cells decrease in emf by about 20 to 40  $\mu\text{v}$  per year. Taking 30  $\mu\text{v}$  per year at  $22^{\circ}\text{C}$  as the rate of decrease and doubling the rate for every  $12^{\circ}\text{C}$  increase in temperature, leads to a rate of 120  $\mu\text{v}$  per year at  $46^{\circ}\text{C}$ , 240  $\mu\text{v}$  per year at  $59^{\circ}\text{C}$ , which is near the upper limit of operation for a 12½ per cent amalgam. If the cell were stored for a year at  $59^{\circ}\text{C}$ , the EMF would be about 0.024 per cent lower at the end of that time. Therefore, to maintain 0.01 per cent accuracy, about 5 months would be the expected life at  $60^{\circ}\text{C}$ . On the other hand, a few hours at  $80^{\circ}\text{C}$  does no permanent damage. The cell should not be expected to be accurate for several days after such overheating, however, and should be carefully checked and recalibrated before being regarded as reliable to 0.01 per cent.

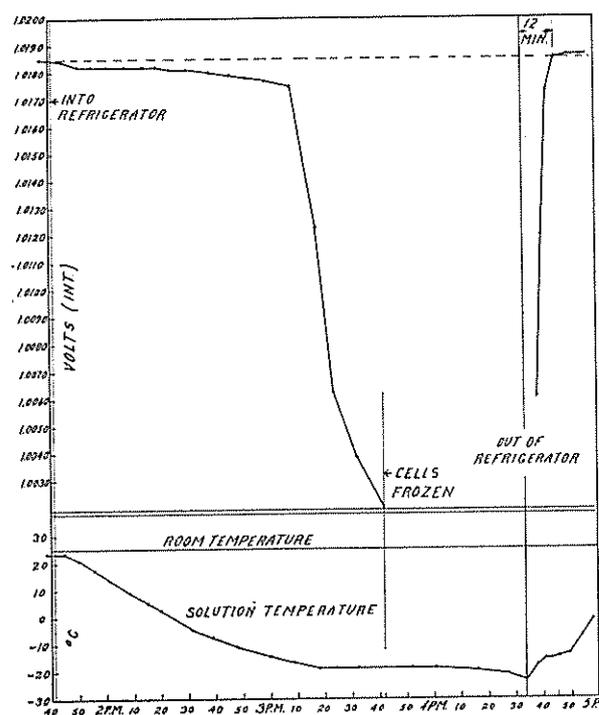


Fig. 6—Freezing and recovery from freezing, unsaturated standard cells.

#### TRANSIENT EFFECTS OF TEMPERATURE CHANGES

Thus far only the effects of temperature on the cells when at equilibrium have been discussed. In addition there must be considered the temporary, transient effects of changing temperature on the emf of cells. These effects are often referred to as hysteresis. Almost every chemical and physical aspect of the cell contributes in some manner to the delay in reaching the final, equilibrium value of EMF for a given temperature.

It must be understood that the temperature coefficient of a standard cell, whether the  $-50$  ppm per  $^{\circ}\text{C}$  of the saturated, or the  $-3$  ppm of the unsaturated form, is the sum of the two opposed coefficients of the limbs, each greater than 300 ppm. Therefore any difference in temperature of the two electrodes will cause large deviations in the emf of the whole cell. Such temperature differences may originate from a nonuniform temperature environment caused by drafts, radiators, circulatory streams in oil thermostats, etc. [13]. However, temporary deviations of EMF are also frequently observed when a cell is moved from one uniform temperature environment to another uniform environment at a different temperature. These deviations result from temporary temperature differences between the electrodes caused in turn by the different heating or cooling rates of the respective electrodes. Since no effort is made to equalize the heat capacities of the two electrodes, it would be pure accident if they were equal. Perhaps attention should be directed to this.

However, such effects are usually of quite short duration, necessarily disappearing when both limbs of the cell are in equilibrium with the same ambient tempera-

ture. Those persistent hysteresis effects, which cause deviations in EMF after the change in temperature of the cell is complete, are often the result of many interacting effects. In saturated cells the reestablishment of equilibrium between solid  $3 \text{ CdSO}_4 \cdot 8\text{H}_2\text{O}$  crystals and the solution is an important factor [30]. In all types, equilibrium between solid  $\text{Hg}_2\text{SO}_4$  and the solution must be reestablished. The septa in portable cells may contribute to hysteresis by furnishing substances which retard the system, especially the mercury electrode, from regaining stable equilibrium [18], [31]. The mere existence of dividing barriers slows down circulation. The presence of free acid reduces hysteresis, and conversely, all materials which tend to reduce, by absorption, neutralization, or other means, the concentration or activity of the free acid tend to increase hysteresis. Even the glass of the container contributes to that effect. In cadmium standard cells hysteresis is always much greater after a decrease than after an increase in temperature. Usually any abnormality of the EMF of the cell disappears immediately upon increasing the temperature again. The more the abnormality has dissipated with time, the less elevation of temperature is necessary to remove it.

#### CONSTANT TEMPERATURE DEVICES

Thermostats are usually used only for saturated cells. Occasionally, when unusually severe changes in ambient temperature, or excursions of the surrounding temperature outside the operating limits of cells are encountered, it becomes necessary to place unsaturated cells in environments provided with controlled heating or cooling, but these are exceptional cases.

Two constant temperature devices are used for maintaining saturated cells, the oil bath [32] and the double-box air bath [33].

The oil bath gives the best results, provided it is properly designed for standard cells. It must have a thermoregulating system capable of maintaining a constant temperature at least to  $0.01^\circ\text{C}$ , and there must be no temperature gradient between the parts of the cells as great as  $0.001^\circ\text{C}$ . If the cells are to be measured to  $0.1 \mu\text{v}$ , they must not vary more than  $0.002^\circ\text{C}$ , which may require damping out of the temperature variation due to the regulating cycle of the bath. Enclosure of the cells in double-walled copper containers, baffling to prevent direct flow of oil from the heater to the cells or cell box, and adequate stirring are required to meet these conditions. If the bath is to be operated at  $28^\circ\text{C}$ , cooling may be needed in summer weather. Fig. 2 illustrates a bath containing these features. The oil is a light grade of mineral oil.

The double-box air bath, which must operate above room temperature, is quite convenient for maintaining saturated standard cells to 0.001 per cent. It is less messy and more easily moved than an oil bath. It consists of a heavy aluminum box, in the walls of which are immersed, in holes, a mercury thermometer and a mercury-in-glass thermoregulator. In an adjacent com-

partment are relays, pilot lights, transformer, etc., as required to control the electric heaters, which are applied to the surfaces of the aluminum box. Enclosed in that box, and thermally insulated from it, is another aluminum box, in which are the cells. The entire apparatus is usually encased in a wooden box, and provided with a binding post panel which connects to the cells within.

#### TIME

##### *Saturated Cells*

The effect of the passage of time upon saturated standard cells, after they have been completely aged, certainly must be described as negligible. There are cells in use at the National Bureau of Standards which are at or near the half-century mark in age, and the working standards at The Eppley Laboratory, Inc., are more than thirty years old. It is true that from time to time a cell becomes erratic or unreliable, and must be removed from a group of standards. However, this happens at all ages of cells, and although such failures are not completely explained and understood, there certainly seems to be little correlation between failure of saturated cells and their ages.

Saturated cells are usually allowed to age for a year before they are considered to be at constant EMF.

##### *Unsaturated Cells*

In the case of unsaturated cells, there is a definite effect of time, which is interrelated with temperature, and has been discussed in connection with the upper limits of storage and operation. For the ordinary laboratory standard, used and stored at normal room temperature, recertification at intervals of one or two years is required to maintain 0.01 per cent accuracy.

#### VIBRATION AND MECHANICAL SHOCK

Standard cells, if made with restraining plugs to keep the electrode materials in place and properly packed as delicate apparatus, can withstand the shocks of normal shipment. It has been found that they will best survive mechanical shock when in the normal, upright position; the least, when inverted. The cells with low internal resistance, having larger electrode masses and larger areas supported only by fabric, are the least rugged. A special mounting of an especially ruggedized Eppley miniature cell has been devised by the Naval Ordnance Laboratory which results in a unit which can withstand such severe shock as a 30-inch free fall onto solid concrete.

Vibration usually has a negligible effect upon the EMF of a standard cell, when an ordinary dc galvanometer is used as the null detector. However, it has been determined that if there is a droplet of free mercury loose in the electrolyte of the cell, a disturbance of that drop, as by jarring, will cause an EMF like a damped oscillation to appear upon the standard cell output. In test cells deliberately made with considerable free mercury loose in the electrolyte, this wave reaches amplitudes as high

as 0.1 v. The period of the oscillations is in the order of 0.01 second; the total duration of a set of waves about 0.1 second. (See Fig. 7.) A device to minimize the occurrence of free mercury in the electrolyte portion of a cell has been patented [34]. The phenomenon would not be disturbing except in a system with short response time.

Visual inspection usually suffices to determine whether a cell has been damaged by mechanical shock.

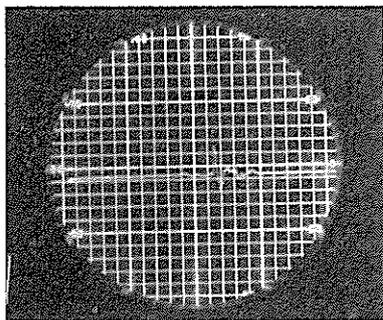


Fig. 7—Cathode ray oscilloscope trace, EMF vs time, disturbance of emf from jarring "loose" mercury in a standard cell. Time, left to right, 1 division = 0.02 second. EMF, vertical, 1 division = 0.01 volt.

One should look for broken leads, especially at the point where the platinum wire enters the glass, for displaced plugs, for mixing of the mercury with the depolarizer paste, and for air bubbles under the negative plug. If none of these defects are observed after mechanical shock, the probability is high that the cell is undamaged. Of course, nothing can take the place of a series of emf measurements against a reliable standard over several days to give assurance of stability.

#### EFFECT OF POSITION

Saturated cells, intended for use as highest grade standards, are made without restraining plugs or septa to keep the materials in place in other than a normal, upright operating position. It is therefore recommended that a saturated cell never be inclined more than 10° from the upright position.

Any less stringent recommendation admits the possibility of permanent damage to the cell by mixing of the materials therein. However, practical experience has shown that some latitude can be taken in the transporting of cells, with no damage resulting. Hand carrying under personal supervision is necessary, but such motion as is occasioned by the normal movement of the arm in carefully carrying the package, or the jarring, bumping, and jiggling encountered in automobile, rail, and air travel have not, in scores of trips, resulted in any cell being damaged. After moving a group of cells, to the NBS for calibration, for instance, it is well to inspect them to be sure none have been damaged. If the mercury-mercurous sulfate interface is reasonably sharp, say, not over 5 mm of mixed portion; the amalgam is entirely below the crystal layer, with no drops or puddles of liquid phase among the crystals; the electrolyte is free of any cloudiness or patches of mercurous

sulfate; the glass container unbroken, especially at its upper tips and around the seals of the leads; and the platinum leads unbroken in their external portion, then there has probably been no mechanical damage wrought upon the cell.

#### Unsaturated Cells

In the so-called portable cells, which, as made in the U.S.A. are the unsaturated type, inversion in shipping does no harm, unless massive shocks occur also. Position becomes important rather in relation to use of the cells. Obviously, if the cell is inverted so that the electrolyte runs away from the electrodes, leaving them isolated from each other, the internal resistance of the cell becomes nearly infinity and the cell inoperative. Depending upon the mechanical details of the construction of the cell, the amount of tipping which can be tolerated without increasing the internal resistance to an undesirably high value will vary quite widely. Practically every type of cell can be operated at 45° inclination to its normal position. Some are now available which will operate at 90° from normal, and a combination of two cells in parallel, mounted at 180° from each other, can be used in all positions. If the individual cells of such a pair are carefully filled so that even in the inverted position they cannot entirely open circuit, they will charge and discharge into each other so that no change in the terminal EMF (in terms of 0.01 per cent) will be observed on rotating the unit a full 360° from its normal position.

It is recommended that the ordinary portable standard cells, not especially designed for use in unusual positions, not be stored in other than the normal upright operating position. There is always the possibility that the amalgam might run away from the platinum wires, or that the isolated electrodes might not be in equilibrium after long separation from the body of the electrolyte. Certainly inversion for a few days would do no great harm, unless the temperature at the same time were high enough to increase greatly the fluidity of the amalgam, say above 40°C.

#### INTERNAL RESISTANCE

The internal resistance of a standard cell is the sum of the resistances of the lead wires, the metallic electrodes, the paste of depolarizer moistened with electrolyte, and the electrolyte. The electrolyte offers by far the largest portion of this resistance, and the characteristics of the internal resistance of the cell therefore are like the characteristics of the resistance of the electrolyte. The temperature coefficient of internal resistance is negative, about -2 per cent/°C near room temperature, and increases sharply at the cryohydric temperature as the electrolyte solidifies.

#### Saturated Cells

The internal resistance of commercial saturated standard cells is usually in the range of 300 to 1000 ohms

at 25°C, although design and methods of manufacture could alter the range quite widely. If a gas bubble forms over the amalgam, and it does not find its way up through the crystals above the amalgam, the internal resistance of the cell will increase, even completely open-circuiting the cell in time. Usually this phenomenon is accompanied by a decrease in the EMF of the cell, which probably is the result of lowered acid concentration in the small bit of electrolyte left in contact with the amalgam. The acid concentration cell so formed between the lower acidity on the negative electrode and the higher acidity in the main body of the electrolyte and at the positive electrode has an EMF in opposition to the main cell EMF.

Often such gas bubbles can be jarred out of the crystals by judicious tapping, as with a lead pencil, and careful orientation of the cell while tapping to permit the gas bubble to find an upward path of escape between the crystals. When this release of entrapped gas is successfully accomplished, the EMF and internal resistance of the cell usually return immediately to normal.

If a cell is measured and certified, as for instance, against the NBS standards, with an entrapped gas bubble in it, and subsequently, perhaps on the return journey, the bubble jars out, the value of the cell may well change by several microvolts, which would render the certification useless, or worse, deceptive. Therefore, it is desirable to inspect cells carefully for bubbles before taking them to be checked, and if any are found, to tap them out, even in the light of the slight accompanying risk of breakage.

#### *Unsaturated Cells*

In unsaturated cells any gas which is formed over the amalgam will collect under the plug and septum in the negative limb. In the past the termination of the useful life of industrial standard cells has often been due to the increased internal resistance resulting from such gas bubble formation. Careful adjustment of the free acid, and improvements in the purification of the cadmium used in the amalgam have practically eliminated this defect.

In case one does have an unsaturated cell with a gas bubble under the negative-side plug, remedial action may be attempted, by tapping the negative limb of the cell on a block of soft wood, while watching the position of the bubble under the plug and trying, by movement of the cell, to manipulate the bubble into a position where some of it can be jarred through the more open portion of the septum.

Although it is seldom possible to remove all the accumulated gas, the bubble and therewith the cell resistance usually can be reduced sufficiently to regain most of the original sensitivity. Occasionally the glass tube is broken or the plugs inside the tube jarred loose, ruining the cell completely. However, if considerable gas is trapped under the plug, the cell is of little value anyway.

#### PASSAGE OF CURRENT

Every use of standard cells involves some passage of current. Within reasonable limits it appears, as might be expected, that the effect of current passage through a cell is related to the product of the current by the length of time for which it flows, or the quantity of electricity moved through the cell. As a result, relatively large currents can be passed for short periods without lasting damage. A momentary short circuit, or a reversed connection to a potentiometer, which may cause twice the short-circuit current to pass, is unlikely to have any lasting effect, even on a high precision standard [35]. Of course, in a saturated cell which is serving as a parts-per-million standard, the temporary effect of such a mischance is significant. Observation against other reliable standard cells over a period of time is the way to be sure that the cell has recovered, but if that is not possible, a four-hour rest would ordinarily be sufficient for recovery to within two ppm of a cell accidentally short-circuited for five seconds or less.

Continuous current drain is sometimes required in modern circuitry, usually in applications requiring lower accuracies, therefore unsaturated cells are generally used. For estimation of expected life and performance, one  $\mu\text{a}$ , flowing continuously for one year, discharges 31.5 coulombs. The figure of  $11 \mu\text{v}/\text{coulomb cm}^{-2}$  may be used to calculate the decrease in EMF per coulomb of discharge per square centimeter of electrode area. When the EMF has decreased about 5 mv, the cell becomes useless as a standard [24].

Passage of current in the charging direction through a standard cell usually has more effect on the EMF than an equal discharge current [36]. As a result, the EMF of a standard cell rises while an ac current is passing through it, although an ac current as great as 1 ma affects the cell EMF by less than 10  $\mu\text{v}$  one minute after it has been interrupted.

If a charging current passes through a cell for long enough to produce a visible amount of mercurous sulfate, the salt formed will be a yellow basic salt, as the conditions do not permit the electrolytic production of the normal salt. The first visible change will be at the boundary between the mercury and the mercurous sulfate, where a dull grayish band perhaps 1 mm wide will form. The appearance of this band, or of a growth of yellow salt in or on the depolarizer paste, are indications that a cell has had a damaging charging current passed through it.

Growth of needles of cadmium from the amalgam are also sometimes seen in cells that have been charged for a long time. The EMF is abnormally high. If damaging discharging currents have been passed, the mercurous sulfate may be partially consumed, crystals of  $\text{CdSO}_4$  may be seen in the negative limb, the cadmium amalgam may be liquified, and the EMF will be abnormally low. These inspection criteria apply particularly to unsaturated cells.

## CLARK CELLS

The zinc cell, proposed by Clark [37] in 1872 and improved in 1884 [38], is similar to the cadmium cell except that wherever we find cadmium or cadmium sulfate in the one, we find zinc or zinc sulfate in the other. Historically, the zinc cell came first, having served as an international standard reference from 1893 until 1908, when it was supplanted by the cadmium or Weston cell.

The temperature formula between 0°C and 30°C has been given as  $E_t = E_{15} - 0.00119(t - 15^\circ) - 0.000007(t - 15)^2$  [39-40].

In 1893 the value 1.434 International volts was assigned as the EMF of the Clark cell at 15°C; Jaeger's value of 1.4328 International volts is now accepted as the best value. Converted, this value is 1.4333 absolute volts. Changing the reference temperature to 28°C leads to the following equation, which is useful in working with present units and practices:

$$E_t \text{ (volts)} = 1.4166 - 0.00137(t - 28^\circ) - 0.000007(t - 28)^2.$$

The difficulties with the Clark cell are gas formation, breakage due to Zn-Pt alloy forming and expanding the Pt wire in the glass wall, high temperature coefficient of emf, and a crystal transition,  $\text{ZnSO}_4 \cdot 7\text{H}_2\text{O}$  to  $\text{ZnSO}_4 \cdot 6\text{H}_2\text{O}$  at about 39°C.

The first of these difficulties is the most serious, especially since with the large change in the solubility of  $\text{ZnSO}_4$  with temperature, there is a tendency for the crystal mass in a cell to form a solid plug. Such plugs keep the gas from escaping to the space above the electrolyte, where it would be harmless.

Proposals to eliminate failures from the second cause have included expanding the Pt wires by alloying them with Zn before sealing the wires into the blanks [41], and changing the design of the tube to increase the distance between the seal and the Zn amalgam. Modern advances suggest the use of plastics such as tetrafluorethylene polymer, which could deform to accommodate the expansion of the wire, or hard glass with tungsten leads which might not expand in contact with the Zn amalgam.

The high-temperature coefficient and rather low crystal transition temperature require closer control of temperature and limit the range of use, but do not rule out the use of the zinc cell.

A consideration of the temperature curves of the zinc and cadmium cells indicates that a combination of 26 to 30 saturated cadmium cells in series, with one saturated zinc cell in series opposition, would result in a battery having an EMF from 25 to 29 volts and an extremely small temperature coefficient of emf at ordinary room temperatures. Table II gives the net EMF and average temperature coefficient of three selected combinations, in absolute volts, calculated from the International temperature formula for the cadmium cell and the above formula for the zinc cell.

TABLE II  
VOLTAGE AND TEMPERATURE COEFFICIENT OF SATURATED  
CADMIUM AND ZINC CELL COMBINATIONS

Cell Combination	30 Cd—1 Zn	28 Cd—1 Zn	26 Cd—1 Zn
EMF at 25°C, absolute volts	29.1319	27.0951	25.0582
Average Temperature Coefficient per cent per °C			
15°-20°C	+0.00054	+0.00084	+0.00120
20°-25°C	-0.00021	+0.00011	+0.00048
25°-30°C	-0.00078	-0.00044	-0.00005
30°-35°C	-0.00121	-0.00086	-0.00045

## LOOKING AHEAD

As mentioned in the introduction, the time is at hand when advances in accuracy of determination of fundamental standards will require improved standards of reference. Whether discovery of a new standard, or refinement of the cadmium standard cell will provide the means for that improvement cannot now be foretold [42].

But aside from the primary standard of reference, secondary standards of EMF are now required which will necessitate advances beyond the limits imposed by the characteristics of today's standard cells.

Work in extreme climates requires standards which will remain operative over such ranges as -80°C to +80°C; rocket-borne standards must withstand tremendous accelerations; the developments of industry need a standard which can supply larger currents without error; the need for a standard of about 0.1 volt for thermocouple work, which has not been satisfactorily filled for more than 20 years, has been joined by a need for a millivolt standard in biological measurements.

We must turn again to the almost endless possibilities that lie in the electrochemical combinations, using the new understanding, techniques, and materials that were unavailable a decade ago.

Perhaps a very simple system, two elements and a binary salt of them, for instance, in a solid electrolyte cell [43], will provide a fulfillment of some of the present needs. Perhaps electrodes consisting of single crystals of very high purity metals will free us from the limitations of amalgams. At the same time, through electronics, the voltage regulator tube and the Zener diode [44] provide other approaches, at least to secondary standards.

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