Standard Cells
Their Construction, Maintenance, and Characteristics

Walter J. Hamer

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Foreword

Accurate measurement of electromotive force is important in many areas of science and technology. Physical standards for such measurement are provided by standard cells, which are electrochemical systems of highly stable electromotive force.

This publication gives the origin and derivation of the unit of electromotive force and outlines procedures by which the National Bureau of Standards maintains and disseminates this unit in terms of standard cells. Information is also given on the construction, maintenance, and characteristics of standard cells as well as a history of their development. Emphasis is placed on precision and accuracy of electromotive force measurements; the stability of standard cells, particularly those of the National Reference Group; and efforts made to construct standard cells of superior quality.

A. V. Astin, Director
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Standard Cells
Their Construction, Maintenance, and Characteristics
Walter J. Hamer

This Monograph contains information on the construction, maintenance, and characteristics of standard cells. The effects of temperature, pressure, electric current, light, shock, and vibration on standard cells are discussed. A history of the realization and maintenance of the unit of electromotive force is also included. A record of international comparisons of the unit of electromotive force is presented as well as information on the constancy of the National Reference Group of Standard Cells.

1. Introduction

Standard cells are physical representations of the unit of electromotive force (emf), serve in the maintenance of the unit, and are used as standards with which the emf of other cells and systems and IR drops are compared. Together with standards of resistance (R) they are also used in the measurement of current, I. When measurements of electric power, P, are made in terms of standards for emf (E) and resistance, the expression for power, 

\[ P = E \times I / R, \]

shows the necessity of knowing E accurately, since a small error in the standard for E would produce a percentage error twice as great in the value for the power, P.

Standard cells are electrochemical systems composed of two dissimilar electrodes immersed in an electrolytic solution. They are not intended to supply electric current and, therefore, are of different design from those electrochemical systems which are intended for such purpose. Owing to their special use, standard cells are required to meet certain performance criteria and, for precise measurements, to have certain inherent characteristics. They must be reasonably reproducible, exhibit good permanency, possess low emf-temperature coefficients, have a low or moderately low internal resistance, be relatively insensitive to current drains of low magnitude, and, if possible, have an emf of convenient magnitude. Since a standard cell is a physical representation of a unit it is obvious why permanency is of prime importance in a standard cell. The precision with which the emf of standard cells is measured, accordingly, exceeds that normally required for other types of galvanic cells.

2. The Unit of Electromotive Force

2.1. Realization

The practical unit of emf, the volt, is not an arbitrary one but like the other electrical units is derived from the basic mechanical units of length, mass, and time using the principles of electromagnetism with the value of the magnetic constant (the so-called permeability of free space) taken as \(4\pi/10^7\) in the rationalized mksa (meter-kilogram-second-ampere) system of units.\(^1\) It has been customary, following the first use of the term by Gauss\(^9\),\(^2\) to refer to electrical units based on the basic units of length, mass, and time as absolute electrical units.\(^3\) The transition from arbitrary to absolute units began with the work of Gauss\(^9\) in 1833 and of Weber\(^2\) in 1851, who showed that it was possible to measure electrical quantities in terms of mechanical units. Weber pointed out the desirability of making the electrical units consistent with those used in other branches of science and engineering.

The electrical units determined in the cgs electromagnetic (em) system are of inconvenient size for practical use. For example, Sir William Thomson (Lord Kelvin)\(^10\) in 1851 showed that the emf of a Daniell cell was about \(1 \times 10^6\) cgs em units. Even so, a Committee of the British Association for the Advancement of Science in 1873\(^6\) recommended the cgs em system for use both in basic science and practical engineering. However, the practitioners, although they agreed with the desirability of relating electrical units to mechanical ones, objected to the use of the cgs em system of units in practice both because of the magnitudes involved and because they had been using such terms as ohms and volts for their units. Their views prevailed and in 1881 the International Congress of Electricians\(^11\) meeting in Paris adopted the cgs em system of units as the fundamental system and the volt-ohm-ampere system for practical use, with the practical units being made larger or smaller than the corresponding cgs em units by an appropriate power of 10.

\(^1\)This is the Giorgi system\(^1\), which is a part of the Sistema Internationale d'Unites\(^1\) (SI), adopted in a resolution, 11th General Conference on Weights and Measures, Paris, October 1960. Other systems for the basic units of length, mass, and time have been used. These include the millimeter-milligram-second system of Weber\(^2\), the meter-gram-second system recommended by the first committee of the British Association for the Advancement of Science associated to consider electrical units\(^3\), the 1948 international system recommended by the 12th General Conference on Weights and Measures, Paris, October 1954, the ampere-ohm-second system used in England for a time\(^8\), and the cgs electromagnetic-second system\(^6\) (see Appendix I). Weber also proposed a rationalized system wherein the cgs unit of emf was increased by a factor \(\sqrt[4]{4}\) of resistance increased by a factor \(2\pi\) and the unit of current decreased by the factor \(\sqrt[4]{4}\). In all of these, the Giorgi system excepted, the magnetic constant (the permeability of free space) is taken as an unit. Regardless of which system is chosen, the practical system remains unaffected. Additional information on electrical units is given in reference\(^8\).

\(^2\)Figures in brackets indicate the literature references on page 31.

\(^3\)It is unfortunate that the name "absolute" has persisted. It is sometimes wrongly interpreted to imply that there are no errors involved in the measurements or that precision has been attained.
The factors chosen for emf, resistance, and current were:

1 volt (practical unit) = $10^8$ cgs electromagnetic units of emf

1 ohm (practical unit) = $10^6$ cgs electromagnetic units of resistance

1 ampere (practical unit) = $10^9$ cgs electromagnetic units of current.

The factor $10^9$ was chosen for emf since then the emf of a Daniell cell, widely used at that time as a rough standard of emf, became approximately 1 volt. The factor $10^6$ was chosen for resistance, for in this way the value of the Siemens mercury column, already used as a resistance standard, especially on the European continent, became approximately 1 ohm (actually about 0.94 ohm). The factor for the ampere was then fixed as $10^9$ by the requirement of Ohm's law.

The unit of emf, although a most important unit, is obtained from the ohm and the ampere. To date, no direct absolute measurement of emf in the em system of units has been found feasible. Instead its value is established experimentally in em units through Ohm's law and the measurement of the fall of potential produced in a resistance by a current, each of these being capable of determination in absolute measure. The ohm in absolute measure is usually obtained in terms of length and time by means of inductance and frequency. In the Wenner [15] method, a mutual inductor of known dimensions, and thus of calculable inductance, is placed in a suitable circuit containing the resistor the value of which is to be determined, a battery, a galvanometer, and two rotary reversing switches. The primary of the mutual inductor is placed in series with the battery and resistor, and with one rotary reversing switch so arranged as to reverse the connections to the secondary. The secondary of the mutual inductor is connected to the potential terminals of the resistor through a galvanometer and a rotary reversing switch for reversing the connections to the secondary terminals. The galvanometer detects the balance between the induced emf in the secondary and the $I/R$ drop across the resistor. When balance is obtained, i.e., when the galvanometer shows no deflection, $I/R = 4\pi n M$ where $I$ is the current in the resistor, $I'$ the current in the primary, $M$ is the comparable mutual inductance, and $n$ is the frequency of commutation in cycles per second (2 $n$ = a number of reversals per second of the rotary reversing switch in the secondary). The circuit is so arranged that during that portion of the cycle when the primary of the mutual inductor is in series with the resistor, $I' = I$; thus

$$R = 4\pi n M.$$ (1)

Since $M$ is calculated from dimensions with reference to length standards and from the permeability of the medium, and $n$ is measured indirectly in terms of the unit of time, $R$ is given in terms of the basic units of length and time and of the permeability of the space surrounding the windings of the inductor. The overall precision (repeatability) of the method is ±5 parts per million (ppm). For more details, reference [16] should be consulted. The ohm in absolute measure may also be obtained with similar accuracy using a self inductor [17] or with lesser accuracy by measuring the relative rotation of a coil and a magnet or the motion of coil in the earth's magnetic field. Although the latter methods are now obsolete they are mentioned here because of their historical importance in the evolution of the electrical units.

The ohm in absolute measure may also be obtained using a computable capacitor [18]. In this method the evaluation of resistance is based on a nominally 1-pl capacitor whose value in es units may be calculated with high accuracy from its dimensions and thence in em units using the speed of light. This capacitor is then used to calibrate 0.01-pl capacitors, the admittances of which are then compared with that of a 104-ohm shielded air resistor using a special bridge network. A conventional d-c step-down is then used to provide absolute calibration of d-c resistors of low magnitude, specifically 1 ohm. For more details reference [18] should be consulted. The overall precision (repeatability) of the method is about ±5 ppm. Operationally, this method is less involved than the inductance methods and may be used on an annual basis to check on the constancy of the resistance standard.

The ampere in absolute measure is obtained in terms of length, mass, and time with a current balance [19]. In the current balance the electrodynamic force of attraction or repulsion, in the direction between two coils (one movable and one stationary) through which a current is flowing is balanced against the force of gravity $mg$, acting on a known mass, $m$, at a location where $g$ is the acceleration due to gravity. From this force and the measured dimensions of the coils (from which the rate of increase, $dM/dx$, of the mutual inductance between the stationary and movable coils may be calculated) together with the permeability of space in which the coils act, the current is expressed in terms of units of length, mass, and time, where time enters into the calculations through the acceleration of gravity. The overall precision (repeatability) of this method is about ±6 ppm. The ampere may also be obtained...
In these measurements they used a value for gravity of 1/7 ppm lower than that derived from Potsdam. Recent studies have shown that ~13 ppm is a better correction of the value derived from Potsdam. Using this correction,

1 NBS ampere = 1.000012 ± 0.000005 absolute amperes.

Cutkosky [18] in 1961, as a result of studies with precision computable capacitors, found that

1 NBS ohm = 1.0000006 ± 0.0000021 absolute ohms.

He also, by recalculating the results of Thomas, Peterson, Cooter, and Kouer [10] obtained with a Wanner mutual inductor, gave

1 NBS ohm = 0.999997 absolute ohm.

(J. L. Thomas has estimated the uncertainty in this value to be ±0.000005). From these relations for the ohm and using the second relation for the ampere,

1 NBS volt = 1.000013 ± 0.000005 absolute volts.

or

1 NBS volt = 1.000009 ± 0.000007 absolute volts.

The NBS volt, as now maintained by standard cell at the National Bureau of Standards, is the one disseminated. When additional data on the above relations are obtained in the United States and other countries, the International Committee of the Bureau International des Poids et Mesures, Sevres, France, which, by international treaty, has authority to coordinate the standards of measurements in the field of electricity as well as of length and mass, may recommend adjustment in the electrical units. Until then, the units as maintained and disseminated by NBS serve to place laboratories in the United States on the same standard basis, accepted by all nations cooperating in the Treaty of the Meter.

The emf of any or all standard cells could be determined in like fashion. Obviously, such a procedure would be cumbersome and time consuming and if required would be unfortunate, indeed. Absolute measurements are involved, require painstaking work and, therefore, are unsuitable for frequent or routine measurements of emf. To circumvent the necessity for frequent absolute measurements, standard cells 6 are constructed, their emfs are determined in relation to current and resistance in absolute measure, and these cells are then used to maintain the volt; these

5 This value differs by 1.7 ppm from that (1.000002) published by Cutkosky [18]. He has since uncovered an error in this magnitude in the published value.

6 Standard resistors, usually hermetically sealed coils of annealed manganese wire 122, are used similarly to maintain the unit of resistance. Owing to the transitory nature of an electric current no physical standards for an ampere have been, to date, possible. Instead the standard ampere is given by the ratio of the values for the standard cell and the standard resistor.
cells are also used to assign emfs to other cells that may be constructed. In other words, the results of absolute measurements are preserved in a physical object, the standard cell. The validity and realization of this approach depends on the possibility of constructing standard cells, the emfs of which are independent (or nearly so) of time; otherwise, the unit of emf would be lost or drift in value in the interval and a repetition of absolute measurements would be imperative at frequent intervals. It is obvious that this matter was and is of critical importance. Over the years extensive work has been conducted to find that electrochemical system which would exhibit constant emfs for long periods of time, say decades. Fortunately, such an electrochemical system (see below under the Weston Cell) has been found. The manner in which the unit of emf is maintained by a group of standard cells is discussed below under maintenance.

2.2. History

In 1893 the International Electrical Congress meeting in Chicago chose the Clark cell, a cell devised by Latimer Clark in 1872 [23], as the standard of emf to which they assigned a value of 1.434 international volts at 15°C in terms of the then accepted standards for the ohm and the ampere. The Clark cell and this value for it were legalized as the standard of emf in the United States by an act of Congress, July 12, 1894 (see Appendix 1). The value, 1.434 international volts at 15°C, followed from the determinations made by Rayleigh and Sidgwick [24], Carhart [25], Kahlé [26], and Glazebrook and Skinner [27] who used current balances or silver coulometers (the electrochemical equivalent of silver having been determined by absolute methods) to determine current and B.A. coils or Siemens mercury columns (or British legal ohms) (known in cgs em units) as standards of resistance. Their results are summarized in Table 1. In each case, the results were converted to a common international basis (see Appendix 1 for the defined international units). The emf-temperature formula of Lord Rayleigh [24, 29] which was then available was used to convert all the values to a temperature of 15°C. The values were referred to as “international” because international agreement had been attained; it was also realized at the time that additional work would be needed to place the values on a basis truly representative of the theoretical cgs em units.

In the years immediately following 1893 most countries adopted 1.434 V for the emf of the Clark cell at 15°C. Later work showed that cells made with specially purified mercurous sulfate (see below for a description of the Clark cell) had an emf 0.0003 V lower than 1.434 V obtained for cells made prior to the meeting of the Chicago International Electrical Congress. Germany, however, in 1898 recommended and adopted 1.4328 V at 15°C for the Clark cell based on the German values for the ohm and ampere. Although the German value was not universally accepted, it was a more nearly correct value as later experiments showed. Also during the years 1893 to 1905 the standard cell devised by Edward Weston [30] was found to have many advantages over the Clark cell and at an informal international conference called by the Physikalisch-Technische Reichsanstalt at Charlottenburg in 1905, the Weston Normal Cell (see later for description) was first proposed as a standard to be used for maintaining the volt and was officially adopted in 1908 at the London International Conference on Electrical Units and Standards [31].

This London Conference went further and adopted provisionally 1.0184 V as the emf of the Weston Normal Cell at 20°C and recommended for the emf-temperature coefficient of the Weston Normal Cell the formula based on the measurements of Wolff [32]. The London Conference still felt, however, that further work was needed and recommended that additional experiments be made.

### Table 1. Absolute Measurements of the Electromotive Force of the Clark Cell

<table>
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<tr>
<th>Experiments</th>
<th>Temperature</th>
<th>Resistance unit</th>
<th>Current method</th>
<th>Expected voltage (at observed temperature)</th>
<th>International values at 15°C</th>
</tr>
</thead>
<tbody>
<tr>
<td>Rayleigh and Sidgwick</td>
<td>15.0</td>
<td>B.A. ohm</td>
<td>Current balance</td>
<td>1.4340</td>
<td>1.434</td>
</tr>
<tr>
<td>Carhart</td>
<td>15.0</td>
<td>Siemens ohm</td>
<td>Silver coulometer</td>
<td>1.4324</td>
<td>1.432</td>
</tr>
<tr>
<td>Glazebrook and Skinner</td>
<td>15.0</td>
<td>B.A. ohm</td>
<td>Silver coulometer</td>
<td>1.4337</td>
<td>1.434</td>
</tr>
</tbody>
</table>

* = Carhart [26] later stated that the value 1.434 V was for a mean of two experiments, one at 10°C and one at 17°C; a correction for this does not alter the rounded value of 1.434 V given above for the absolute emf of the Clark cell.

1. B.A. ohm = 0.9966 international ohm.

2. Carhart and Kahlé converted their values from Siemens units to British legal units, using the relation 1 British legal ohm = 1.06 Siemens ohm.

3. 1.118 mg silver deposited per second per ampere (international value of electrochemical equivalent of silver).

4. B.A. volt.

5. British legal volt.

6. 1 British legal ohm = 0.9976 international ohm.
ingly, scientists from England, France, and any met with United States scientists at the annual Bureau of Standards in 1910, and as a result of their experiments with a large number of normal cells and silver-coulometer determinations adopted 1.0183 V as the emf of the Weston Cell at 20°C. Values derived from this later assumed to be significant to the fifth or seventh decimal as a basis of measurement. This value (1.0183 V) was still characterized as "international" units since the basis on which the new measurements (1910) were made was same as it was in 1893; the precision of the measurements was higher, however.

Values assigned to the reference groups of each rating nation served as the fundamental basis for emf measurements from 1911 to 1948. By after interruptions caused by the two World Wars and other improvements in techniques, an accurate determination of the electrical quantities in emf units was achieved, and on January 1, 1948, changes from international to absolute units officially made internationally. The legal units of these new units in the United States is nearly the same as that of the older ones because of 1894 (see Appendix 1) mentions both sets through "international" and "absolute" are frequently used in referring to the system in the em system of units, and the above terms had significance only during a period in which efforts were being made to achieve the theoretical unit, and therefore, of only one kind of volt, when the term used, "absolute volt" is implied, i.e., the volt has a direct relation to the standard.

of units on an equivalent basis. However, in order to remove the ambiguities of the old act, new legislation was passed by the Congress in 1950 (see Appendix 2). The changes 1351 for the United States were:

1 international volt (US) = 1.000330 absolute volts
1 international ohm (US) = 1.000495 absolute ohms
1 international ampere (US) = 0.999925 absolute ampere
1 international coulomb (US) = 0.999835 absolute coulomb
1 international henry (US) = 1.000495 absolute henries
1 international farad (US) = 0.999505 absolute farad
1 international watt (US) = 1.000165 absolute watts
1 international joule (US) = 1.000165 absolute joules

The conversion factors in other countries were nearly the same as these. The emf of the Weston Normal Cell at 20°C on the new basis then became 1.01864 V. This value is now of historical interest only.

The relation of the fundamental units to the measurement of power and energy in both the new and former systems of units is shown diagrammatically in figure 1. The left half represents the fundamental units and standards maintained by the National Bureau of Standards, the right half the units and standards used by the public.

2.3. Maintenance

The unit of electromotive force in the United States was originally maintained (1897-1906) by seven Clark cells, the mean of which was assigned a value at 1.433 V (this value was 0.0003 V lower than the value recommended in 1893 by the

Figure 1. Diagram showing the relation of the present and former systems of electrical units to the basic mechanical units of length, mass, and time.

5
Chicago International Electrical Congress because specially purified mercuroxy sulfide had been used in the preparation of the cells; it was 0.0009 V higher, however, than the value then recommended by Germany). In 1906 the standard consisted of both Clark and Weston Normal cells and after 1908 of Weston cells only; an emf of 1.019126 V was assigned to the mean of the Weston cells at 20°C based on a direct comparison with the Clark cells (on the German basis the emf of the Weston cells was 1.018226 V which was only slightly lower than 1.0183 V found in 1910 by the International Committee which met at the National Bureau of Standards). After 1911, this latter unit was maintained in each country until 1948 when "absolute" units were adopted. The number of cells constituting the national standard has varied from time to time; when a cell shows a steady change from its previously steady value it is removed from the group (see later for criterion and procedure).

Today, the National Reference Group of Standard cells consists of 44 saturated Weston (or cadmium sulfate) cells, all of which have been made at the National Bureau of Standards from highly purified materials and assembled under controlled conditions (see later for details). The National Standard is based on the mean emf of these 44 cells. The emf of any one cell in the group is equal to the mean emf, less the average deviation in emf of all 44 cells from the emf of a selected reference cell in the group, plus the deviation in emf of the individual cell from that of the selected reference cell, or

\[ E_c = E_m - \frac{\Sigma \Delta}{44} + (E_c - E_r) \]  

where \( E_c \) = the emf of an individual cell, \( E_m \) = the mean emf of the 44 cells, \( \Sigma \Delta \) = the algebraic summation of the differences between the emf of a selected reference cell, \( E_r \), and the emfs of all of the other cells in the group. This reference group (of cells) consists of three parts, of 11 "neutral" cells made in 1906, 7 "acid" (0.05N) cells made in 1933, and 26 "acid" (0.05N) cells made in 1948. The last two groups of cells were added to the reference group in 1937 and 1955, respectively. The meaning of the terms "neutral" and "acid" appears later. This National Reference Group of cells is also supplemented by a group of cadmium sulfate cells made with 98 percent deuterium oxide (heavy water) [36], the emf of which is about 380 \( \mu \)V lower than that of cadmium sulfate cells made with normal water. These cells are discussed in Appendix 3, but suffice it to say here that a study of the ratio of the emfs of cells made with normal and heavy water offers an auxiliary check on the stability of the national unit of emf.

Obviously, all of a group of "identical" cells may increase or decrease in emf with time without departing from the original assigned mean becoming evident. Therefore, an alternative type of standard cell of approximately the same emf as the Weston cell\(^8\) but of different composition would be most valuable, for if changes in emf with time in two different systems occurred, they would not be likely to follow the same pattern. Thus studies of the ratio of emfs of two different systems over a period of years would give valuable insight into the stability of the standard. It is for this reason that the National Standard or Reference Group was eventually designed to include "neutral" and "acid" cells \(^8\) and to be supplemented by cadmium sulfate cells made with heavy water. The ratio or the difference between the emfs of "neutral" and "acid" cells is followed in the course of maintaining the unit of emf.

A cell is removed from the reference group when its emf has drifted by more than 1.0 \( \mu \)V from its previously steady value. When a cell is removed, the mean emf of the group is "recaptured" by reverting in the records to the time the cell had been added to the reference group, calculating a new mean for the reduced group (less the cell removed) at that time, and finally carrying the new mean forward. In some cases it has entailed going back as much as 20 years. Since the cells have closely agreeing emfs the removal of one cell has only a minor effect on the mean emf of the group; this effect has generally been below 1 \( \mu \)V. The effect on the emf of the mean of removing one cell obviously is smaller the larger the number of cells in the group (for practical reasons there is a limit to this number; if too high a number, it might not be possible to measure the emfs of all the cells within any one day—this would then increase the problems associated with maintenance).

It is difficult to provide incontrovertible evidence regarding the long-term stability of the volt maintained with saturated standard cells. A considerable body of evidence indicates, however, that it is very unlikely that the unit of emf preserved with the National Reference Group of Standard Cells has changed by any significant amount in the last 53 years. This evidence follows:

(1) In terms of measurements with silver coulombs (or voltmeters) and standard resistors—prior to 1948 silver coulometers were used in defining the international ampere (see Appendix 1). To date, however, there are no international specifications that enable the coulometer to be used unambiguously as a means of reproducing the international ampere. Even so, experiments repeated with a given type of coulometer under the same conditions after a lapse of a number of years can serve to establish the same current to high accuracy. From 1910 to 1912, inclusive, [37] a series of experiments were made at the National Bureau of Standards with a Smith form of coulometer and the results were expressed in terms of the emf of the saturated Weston cell at 20°C; the average of 55 experiments gave 1.018274 V for the Weston cell at 20°C. In

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\(^{8}\) Cells that differ more or less in their chemical composition than "neutral" and "acid" cells or "normal water" and "heavy water" cadmium sulfate cells would be even more desirable for this purpose. However, to date, the prime requirement of constancy in emf has not been as well realized in other systems as it has been in cells of the cadmium sulfate type.
series of coulometer experiments were con-
ducted at the Physikalisch-Technische Reichsan-
stalt by representatives from Germany, Great
Britain, and the United States [34, 38, 39]; the
results obtained by the United States with the Smith
& Wesson coulometer gave 1.018278 V for the Weston
20°C. Assuming that the unit of resistance
changed during this interval of time the
indicate that the drift in the unit of emf was
about 0.05 μV per year.

In terms of measurements with current balances and
standard resistors—In 1934 Curtis and Curtis
reported a current balance originally used by Rosa,
Roberts, and Miller [41] that 1 NBS interna-
tional ampere (given by ratio of NBS units of emf
existance) was equal to 0.999920 absolute
e, whereas the results of Rosa et al. in 1911
0.999926 absolute ampere. Accordingly,
posing that the resistance did not change,
results indicate that any apparent drift in the
emf could not have exceeded 0.1 μV per
year. Also, since 1932, all checks of the NBS unit
have agreed within the precision (± 7 ppm)
by solute measurements with current
apparatus or eddy current meters and self or
self inductors; these checks indicate that the
emf is constant to ±0.2 to ±0.3 μV per year
unit of resistance has remained unchanged.
In terms of the gyromagnetic ratio of the
in these experiments the precession
ability, as stated above, is measured in a
atic field known in terms of the absolute
e and the constant of an accurately made
The solenoid current, when compared
given by the ratio of the NBS standards of
and resistance, has been found to have the
to better than 0.1 μA during the interval
January 1960 to March 1963. If the unit of
ince remained constant during this period,
emf has also remained constant to better
0.1 μV per year. The construction and prop-
of standard resistors and standard cells are
different; the possibility that the two
should drift in such a manner as to maintain
stant ratio seems remote. The accuracy of
ite resistance measurements has increased
cantly in recent times. Modern absolute
ance measurements coupled with reference to
c constants should, in the foreseeable future,
y convincing evidence regarding the stability
resistors and cells.
In terms of "neutral" and "acid" cells—the
ence between the average emfs of the "neu-
and "acid" cells in the National Reference
of Standard Cells has increased by 8.2 μV in
dards, with the increase being only 1.0 μV during
those 10 years [42]. This comparison was made
neutral" and 11 "acid" cells, or for cells of
this type in the National Reference Group since
1937. Since the emfs of "neutral" and "acid" cells
have remained relatively constant during the last
10 years, the earlier drift in their difference may be
attributed to an aging effect exhibited by the "acid"
cells (the "neutral" cells were 26 years old at the
start of the comparison between the "neutral" and
"acid" cells). For the last 10 years the average
change in the emf has been 0.10 μV.

(5) In terms of international comparisons—in 1948
the units of emf of the United States (USA) and the
Bureau International des Poids et Mesures (BIPM)
agreed whereas in 1960 the USA unit was 1.9 μV
smaller than the BIPM unit. Assuming that the
BIPM unit had remained constant during this time
the USA unit has changed at a rate of 0.16 μV
per year. Assuming that the BIPM and USA units
changed at the same rates but in opposite directions
the USA unit then changed at a rate of −0.08 μV
per year. Additional data on international compari-
sions are given in section 2.5.

(6) In terms of customers' cells—customers' satura-
ted cells, shocked in terms of the National
Standard of emf, show, on the average, an
average variation of ±1.2 μV per year, but no drifts in emf in
one direction or the other. This relative stability
reverses only for cells that are about 3 or more years of
age; saturated standard cells usually exhibit an
aging effect of several microvolts during the first 3
years after their construction.

(7) In terms of newly prepared cells—saturated
standard cells freshly made from new materials
usually agree with old or aged cells within 5 μV.
Of course, in this type of comparison the cells must
be made with amalgams of the same percentage
of cadmium and with cadmium sulfate solutions of
the same acidity with respect to sulfuric acid. The
point here is that saturated cadmium cells, made at
different times to essentially the same specifi-
ation, are highly reproducible. Cells made in the
past cannot have drifted seriously in emf if similar
cells of recent construction agree closely in emf with
them.

(8) In terms of the relative emfs of cells within a
group of cells—the differences in emf between the
cells in the National Reference Group of Standard
Cells have remained remarkably constant for de-
decades. Although, as stated above, all "identical"
cells may increase or decrease in emf without evi-
dent departures from their mean emf, constancy
in the difference between the emf of individual cells
in a group of cells with time nevertheless, in combi-
nation with items (1), (2), (3) above, increases
confidence in the constancy of the mean emf of a
group of cells.

Although the above remarks apply to the stability
of standard cells in the National Reference Group of Standard
Cells they should also apply to any
standard cell of the saturated type providing it is a
quality cell properly maintained. Cells made
with impure materials or poorly assembled will invariably
show much less stability in emf. In section 2.5
the need for adjustments in the assigned values to
standard cells, although infrequent, is discussed. The need for these adjustments is not clear. It may be that the cells were of poor quality, were affected by transport, or had not come to equilibrium after temperature changes which are involved in international comparisons.

The standard cells of the National Reference Group are housed in slowly stirred oil baths maintained at 28°C under diffused light in an air-conditioned room maintained at 25°C ± 1°C; the relative humidity automatically remains below 50 percent. The temperature of the baths is maintained at 28°C within ±0.01°C on a long-term basis and within ±0.001°C during measurements using a Gouy controller [43].

In a Gouy controller, a steel piano wire extending into the mercury of the mercury-toluene regulator is connected to a wheel which revolves at a slow rate whereby the wire is made to periodically make and break contact with the mercury. The design of the bath and its temperature control are described in Appendix 5. A special mineral oil, having the characteristics listed in Appendix 6, is used as fluid in the constant-temperature baths. Tests made to determine the temperature of the oil at various locations within the baths indicated a uniform temperature within ±0.001°C, i.e., no hot or cold spots prevail within the bath or in the vicinity of the standard cells. This design follows closely that described many years ago by Wolff and Waters [44]. A bath for use with saturated standard cells has also been described recently by P. H. Lowrie, Jr. [45].

The cells are supported about 2 in. below the surface of the oil on seasoned mahogany strips about 16 mm wide (slightly smaller than the distance between the limbs of NBS H-shaped cells) and about 10 mm thick and either 24 or 48 cm long, with grooves into which the cross-arms of the cells fit snugly. Some racks carry 18 cells equally spaced, except for a somewhat wider space at the middle of the rack where the rack is supported; others carry 9 cells. Hard rubber, bakelite, or lucite strips (widened U-shaped), about 40 mm long, 10 mm wide, and 10 mm thick in the center and 13 mm at each end, are mounted between cells across the underride of the mahogany strip. In the top of each strip, at each end, is inserted a short copper rod provided with a pair of holes, one 1 mm and the other 2 mm in diameter and both about 9 mm in depth; these holes serve as mercury cups, one for each cell terminal and the other for external connections.

These two copper cups are spaced at the same distance apart on each strip, so that any cell can be put in the electric circuit by a stabber consisting of a pair of stiff copper wires mounted in a lucite block (copper wires are amalgamated on the tips). This is a copper-copper connection through the mercury and under the oil. From this point on all contacts are copper-copper to avoid thermal emfs. The other end of the stabber connection goes to a positive position. There are two post positions, one for the Reference Cell and one for the Unknown Cell. The leads of the cells go from the posts through conductors to another post at the emf-measuring instrument (see later), where the two cells are placed in series opposition by joining the negative and the difference is measured.

A photograph showing the oil baths that house the National Reference Group of Cells is shown in figure 2. Other baths of intermediate size are also available for housing cells on test. The temperature of the baths is measured with a platinum resistance thermometer and a Mueller bridge having a sensitivity of 0.0001 ohm, corresponding to 0.001°C.

**2.4. Dissemination**

Comparisons of the emf of standard cells, such as may be required in the dissemination of the unit of emf, i.e., the transfer of the unit from a standardizing laboratory, must be carried out by procedures of the highest precision involving a minimum of uncertainty. In this case, comparisons are made between standard cells, the emf of which have been determined in absolute units and other standard cells, the emf of which have not been so determined. The former may be called reference cells and the latter unknown cells. These intercomparisons may be made with high accuracy with potentiometers by the opposition method (preferably called the difference method). In this method the two cells (reference and unknown) are connected in series with their emfs in opposition and the difference in emf between the two is measured with a potentiometer using a galvanometer of high sensitivity. Because the difference in emf between the two cells is small, only a moderate percentage accuracy in its determination is required to give the emf of the unknown cell accurately in terms of the known reference cell. If the difference between the two cells were 100 μV the accuracy of the measurements need be only 1 percent to give the difference to 1 μV or only 0.1 percent to give an accuracy of 0.1 μV.

This method is not direct reading, however, and
or must determine which of the two cells has the greater emf. The greatest source of errors by the difference method is the thermoelectric action. At the National Standards a special comparator, designed [46], is used. This comparator is designed to compensate for parasitic thermal emfs. Since and unknown cells are connected in series with a galvanometer and a source of a few microvolts and a adjusting device in the auxiliary source until the meter indicates a null balance. The galvanometer (see G, figure 3) is used with a free period of 8 sec, an external resistance of 1200 ohms, and a sensitivity of 1 microvolt at one meter lamp and scale when operated slightly underdamped.

The Brooks comparator, differences in emf is 2100 μV may be read with a precision of 1%. The Brooks comparator contains an circuit for the detection and compensation of thermal emfs in the galvanometer circuit, a sliding part in the main circuit, and an output device by which the measured emf in the emf is added algebraically to the reference cell thereby giving directly the emf of the unknown cell.

Illustrating the principle of the Brooks comparator is shown diagrammatically in figure 3. The comparator contains figures 4 and 5, respectively. The upper three sections shown in figure 3 relates to the measurement of the current in the comparator for a particular value of R. A current I, from battery B, to a cell) is regulated by the rheostat R to a value in the usual manner by reference to the standard cell. All parts with exception of points numbered 3 to 16 are selected as needed. Each step is 100 μV, necessary to interpolate between successive steps of the process of measuring the unknown cell, X (lower section). This is accomplished by the circuits attached to and 18. B2 and B3 are No. 6 dry cells, or milliammeter A measures the current in exact balance is indicated by the galvanometer as a result of varying the resistance R. Milliammeter A is calibrated to make its scale precisely in microvolts. A similar circuit at 1 and 2 performs a like function for the cell N (lower section) whose emf value is determined exactly if the readings for the unknown X and the reference cell, N, are connected in opposition. This circuit also contains the thermocouple G1, of sensitivity, given above.

Emf compensation is achieved by a copper slide wire connected in series with the main galvanometer, G1. About 15 μA from a No. 6 dry cell (not shown in the figure) enters this slide wire at its central point and leaves by a slider. If the slider is set at the central point of the copper wire there is no current in the copper wire and, therefore, no potential drop. By setting the slider away from the central point, a small adjustable potential drop may be introduced into the galva-
nometer circuit to neutralize any parasitic emf in the galvanometer and the wires connecting it to the comparator. By depressing a “shunt” key any appreciable parasitic emf can be detected; if present it will maintain a corresponding deflection of the galvanometer and when the “shunt” key is depressed the galvanometer coil will assume its open-circuit zero position. To neutralize this undesired emf the slider is manipulated until no motion of the galvanometer coil ensues when the “shunt” key is depressed. For additional details the original paper by Brooks [46] should be consulted.

Although compensation for thermal effects is provided in the instrument, thermal effects may also arise at the cell terminals. These are eliminated by making connections to the cells through mercury cups immersed two inches below the surface of oil maintained at the same temperature as the cells, as was mentioned above under maintenance (section 2.3). In those cases (for example, unsaturated cells or saturated cells in air boxes; see later) where the terminals of the unknown cell cannot be immersed in oil, thermal effects are kept at a minimum by using like metal connections in a constant-temperature room. Other types of standard cell comparators have been described by Miller [47], Vincent [48], and by Spinks and Hermach [49].

The comparator (portable potentiometer) of Spinks and Hermach also includes two saturated and two unsaturated standard cells in a temperature-controlled enclosure.

In the dissemination of the unit of emf, i.e., the comparison of unknown and reference cells, working groups of standard cells were used in place of the national Reference Group of Standard Cells. Of course, the emf of the cells within those working groups are known in terms of the National Reference Group. These comparisons are made with a precision of 0.6 μV. One working group is maintained in the Standard Cell Laboratory in Washington, D.C., the other at the NBS Boulder Laboratories in Boulder, Colo. [50]. A total of 10 comparisons of emf of the unknown (customer) cells with the working groups is made, one per day, over a period of ten days, at a specified temperature for saturated cells and at an ambient temperature of 25 C (at Washington) and of 23 C (at Boulder) for unsaturated cells.13 The best saturated cells are calibrated with an uncertainty of 0.0001 percent; the best unsaturated cells with an uncertainty of 0.005 percent. The results are transmitted to customers Reports of Calibration.

2.5. International Comparisons

Since 1932 the units of emf of various nations have been intercompared at specified intervals at the Bureau International des Poids et Mesures (BIPM), Sèvres, France. At the present time this interval is 3 years. For many years the comparisons were ther sporadic, and they were interrupted by the

13 The National Bureau of Standards provides emf calibrations of unsaturated standard cells only for public utilities and others having operations of such a nature as require calibrations by the National Bureau of Standards.

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Figure 6. International comparisons of the unit of electromotive force in international volts prior to 1948.

Two World Wars (see fig. 6). Prior to 1948 the intercomparisons were made in "international volts," and since 1948 in "absolute volts" (see figs. 6 and 7). These intercomparisons are effected by standard cells maintained by the participating countries and by the International Bureau and are conducted at 20 C. As a rule each country submits 4 to 10 cells to BIPM for the intercomparisons; at the present time the cells are carried to BIPM by messenger.

The first comparison involved the measurements at the National Bureau of Standards in 1910, at which time the units of the participating countries—France, Germany, Great Britain, and the United States—were identical (see fig. 6). From 1911 to 1932 the major intercomparisons were between the units as maintained in the United States and in Great Britain. In preparing figure 6 it was assumed that the mean value for these two nations remained constant and this mean is made the axis of abscissas. A few comparisons were also made of the United States unit with those of France, Germany, Japan, and Russia and are shown in figure 6 in terms of the mean unit of the United States and Great Britain. In 1931 it was apparent that there was an increasing discrepancy between the unit as maintained in Germany at the Physikalisch-Technische Reichsanstalt (or PTR) in Charlottenburg and those maintained in the United States at the National Bureau of Standards (or NBS) in Washington, D.C., and in Great Britain at the National Physical Laboratory (or NPL) in Teddington. Consequently, at the invitation of the PTR arrangements were made to have an international committee carry out experiments with the silver coulometer at PTR and thus reestablish the international volt. Accordingly, P. Vigoureux of NPL and G. W. Vinal of NBS took silver coulometers to the PTR together with standard cells and standard resistors, the values of which had been carefully determined at their respective laboratories. At the PTR, these standards were compared with those of the PTR and an extensive series of experiments with different types of...
coulometers were made. As a result of measurements, subsequently published [34, Germany increased its unit by 82 ppm (see for United States data). Result of extensive work on silver coulometers sov [51], Russia changed its unit in 1934 by adjustment; this adjustment made the BIPM unit 2.2 ppm lower than its 1935 unit; the data in figure 6 are so reported. For the last comparison in international volts the National Physical Laboratory submitted cells in 1945 and the comparison with BIPM was completed in 1946; the other countries submitted cells in 1948 and the comparisons with BIPM were done the same year. Russia reported its values in absolute units using the international relation: 1 mean international volt = 1.00034 absolute volts. In 1939 the Russian unit had been 23.1 µV below the mean international unit. For comparisons with other countries and assuming that this difference still applied, BIPM converted the Russian absolute values to international values using a conversion factor of 1.000317.

On January 1, 1948, “absolute” units were adopted but international comparisons on this basis were not made until 1950. Intercomparisons in the “absolute” units, obtained since 1950, are given in figure 7 (note that the scale in figure 7 is much larger than in figure 6); Australia and Canada were new additions. In 1950 the German value was from East Germany while in 1953, 1955, and 1957 both East and West Germany took part in the international comparisons; since 1957 the German value is for West Germany. The data shown in figure 7 are the deviations from the BIPM mean value. In 1950 Russia had apparently corrected their “absolute” values of 1948 by the average deviations of the various countries, Russia excepted, from the BIPM unit, thus, ignoring the fact that their unit had been 23.1 µV below the mean international unit in 1939; this procedure, then placed their unit in 1950 above the BIPM unit by approximately this magnitude. In 1935 Russia made an adjustment in its unit of about 13 µV. In 1960 the spread between the 8 countries was 10.2 µV with the units of Australia, Great Britain, and Russia being high. The spread between the other 5 countries was 3.3 µV. In 1960, values for Italian cells were included with the values listed with the French cells; France had first made a direct comparison of the Italian cells with their cells at the Laboratoire Central d'Electricité, Fontenay-aux-Roses, France.

3. Early Standard Cells

types of galvanic cells have been proposed tardo of cmf and some of thees have ap in a variety of forms. Although Faraday's of his time used various galvanic cells, Grove and Bunsen cells, in their investiga Daniell cell [54] represented by

\[
\text{Zn(s)} \mid \text{ZnSO}_4, \text{H}_2\text{SO}_4(aq) \parallel \text{CuSO}_4(aq) \mid \text{Cu(s)}(+) \nonumber
\]

first cell seriously used as a standard of it exhibited less gassing than its predecessors; a single vertical line is used to indicate a change of two distinct phases, a double line to indicate a liquid-liquid junction, and \(\text{aq}\) = aqueous solution. However, this type of cell did not exhibit a long-term stability in cmf. Being a two fluid cell, the solution diffused into each other causing local action at the electrodes and a steady decrease in cmf. Somewhat better results were obtained when saturated solutions, no acid, and amalgamated zinc were used, but, even so, the cells did not exhibit the permanency required in a standard. Nevertheless, for over 35 years, Daniell cells were used as a standard of cmf. Absolute electrical measurements gave 1.07 to 1.14 V for the cmf of freshly prepared cells; the actual value depended on the concentration and acidity of the solutions used. Absolute measurements were not needed to show the lack of constancy in the cmf of the cells; this
behavior was evident from comparing new cells with old ones. The cell reaction is

\[ \text{Zn(s)} + \text{CuSO}_4(\text{aq}) \rightarrow \text{ZnSO}_4(\text{aq}) + \text{Cu(s)}. \]  

(4)

The Daniell cell has an emf-temperature coefficient of about +34 μV/deg C at room temperature (18 to 30°C).

Daniell cells were made in various forms. The original form consisted of a glass jar containing a porous pot of unglazed earthenware in which a zinc plate or rod was placed. Outside and around the pot a cylindrical sheet of copper was placed. The outer jar was filled with a concentrated solution of copper sulfate and the porous pot with dilute sulfuric acid, or zinc sulfate, or zinc sulfate acidified with sulfuric acid [55]. Important modifications were gravity [50] and Fleming-Thomson cells [37]. In the gravity cell the less dense solution of zinc sulfate was placed over the more dense solution of copper sulfate so that the porous cup was saturated. Zinc in circular or crown-foot form and copper in leaf form were used as electrodes in their respective salt solutions. In practice the cell was kept closed circuit to curtail the mixing of the solutions. In the Fleming-Thomson cell a -tube was used containing a solution of copper sulfate in one arm and a solution of zinc sulfate of the same density in the other arm. Rods of copper and zinc were supported in their respective salt solutions.

In 1872 Latimer Clark [23] proposed a cell which had a profound effect on work pertaining to the electrical units. His cell, represented by

\[ \text{Zn(s)} | \text{ZnSO}_4 \cdot 7\text{H}_2\text{O}(c) | \text{ZnSO}_4(\text{sat aq}) | \text{ZnSO}_4 \cdot 7\text{H}_2\text{O}(c) | \text{Hg}(l) \]

where \( c = \) crystals, \( s = \) solid, \( l = \) liquid, and sat = saturated aqueous solution was a one-fluid cell free of a liquid-liquid junction and exhibited relatively good stability in emf. Because of the storical importance of the Clark cell (see sec. 2) is discussed in more detail in section 4. Owing the success that was obtained with the Clark cell several other one-fluid cells were proposed as standards, the more important being those suggested by De la Rue [58], Helmholtz [59], Gouy [60], and Weston [30]. Of those four the first three exhibit larger drifts in emf and had higher internal resistances than Clark cells, while the last one had any advantages over the Clark cell. As a result, cation cells are now used almost exclusively as standards of emf. Weston cells had an emf-temperature coefficient of 1/10th of that of the ark cell, better emf stability, and an emf closer unity than the Clark cell.

Early types of standard cells are listed in abbreviated form in table 2 together with their nominal af and emf-temperature coefficient. As is evident from the table the Weston cell is similar to the ark cell except that Cd replaces Zn. In all of these cells, the original Clark cell excepted, amalgamated anodes were generally recommended and H-shaped containers (see below) were frequently used. In general, saturated solutions were used and excess crystals of the stable salt added to the cells at the electrode surfaces. Weston [61] and Carhart [62] proposed the use of an unsaturated solution of zinc sulfate in the Clark cell in order to decrease its emf-temperature coefficient. The original Weston patents also covered the unsaturated form of Weston cell.

**Table 2. Early types of standard cells**

<table>
<thead>
<tr>
<th>Name</th>
<th>Date</th>
<th>System</th>
<th>Approximate emf, volts</th>
<th>Approximate dE/dT, volts per deg C</th>
</tr>
</thead>
<tbody>
<tr>
<td>Daniell</td>
<td>1836</td>
<td>Zn</td>
<td>ZnSO₄</td>
<td>CuSO₄</td>
</tr>
<tr>
<td>Clark</td>
<td>1872</td>
<td>Zn</td>
<td>ZnSO₄</td>
<td>H₂SO₄</td>
</tr>
<tr>
<td>De la Rue</td>
<td>1877</td>
<td>Zn</td>
<td>ZnSO₄</td>
<td>H₂SO₄</td>
</tr>
<tr>
<td>Helmholtz</td>
<td>1882</td>
<td>Zn</td>
<td>ZnSO₄</td>
<td>H₂SO₄</td>
</tr>
<tr>
<td>Gouy</td>
<td>1888</td>
<td>Zn</td>
<td>ZnSO₄</td>
<td>H₂SO₄</td>
</tr>
<tr>
<td>Weston</td>
<td>1892</td>
<td>Cd</td>
<td>CdSO₄</td>
<td>H₂SO₄</td>
</tr>
</tbody>
</table>

(a) represents nominal value at room temperature (about 18 to 30 °C).

Somewhat later Brönsted [63] proposed the cell:

\[ (-)\text{Pb}, \text{Hg}(l)/\text{K}_2\text{SO}_₄\cdot\text{PbSO}_₄(\text{sat aq})/\text{K}_2\text{SO}_₄(\text{aq})/\text{Hg}(l)(+). \]

as a standard, stating that at 22 °C it had an average emf of 1.0481 V and an emf-temperature coefficient of -0.0001 V/deg C. Henderson and Stegeman [64], however, stated that the Brönsted cell did not exhibit steady emfs with time and that better results were obtained when Na₂SO₄ was used as the electrolyte. However, their cell at 25 °C had a lower emf of 0.9440 V and a higher emf-temperature coefficient of +0.000174 V/deg C. These cells have not been used probably because of their high emf-temperature coefficients. Vosburgh, Guatavent, and Clayton [65] proposed the cell:

\[ (-)\text{Cd}, \text{Bi}, \text{Hg}(l)/\text{C}_2\text{SO}_₄(0.1 \text{ M acetic acid})/\text{C}_2\text{SO}_₄(0.1 \text{ M acetic acid})/\text{Hg}(l)(+). \]

which is a modified Weston cell in which a 3-phase (3p) amalgam (8.9 percent Cd, 11.1 percent Bi, 80 percent Hg) and a 0.1 M acetic acid or 0.01 M H₂SO₄ solution saturated with the two salts, as indicated, are used. The cells were sealed with a nitrogen atmosphere inside. At 25 °C they reported an average emf of 1.0184 V and an emf-temperature coefficient of +0.000013 V/deg C which is about 2 to 10 times that of unsaturated Weston cells but less than one-third of that of the saturated Weston cell at 20 to 30 °C but of opposite sign. Data available on this cell indicate that it does not have the long-term stability exhibited by saturated Weston cells, but compares most favorably with the unsaturated type [66].
4. The Clark Cell

Above, the original Clark cells contained a zinc anode and a mercury-mercurous sulfate in a saturated solution of zinc sulfide crystals of ZnSO₄ · 7H₂O. Clark's simple construction, as shown by (a) in the figure, was used in commercial cells; one such cell being the British Board of Trade cell 1 by (b) in the figure. In all of these cells, the zinc was in contact with the paste consisting of sulfide, a saturated solution of zinc and crystals of ZnSO₄ · 7H₂O.

Determined the emf of his cell in absolute in (a) a zinc galvanometer and (b) an electrometer and a B. A. resistor (see footnote 7). With these he obtained 1.45735 V and 1.457, respectively, at 15.3 °C, the mean of rounded to 1.457 V as the absolute emf of Clark's cell, although much better as a than the two-fluid cells, did not show the they in emf hoped for. The cell tended to because the anode and the emf showed large owing mainly to concentration gradients that developed, during slight changes in ambient temperatures, within the compact paste.

In 1884 Rayleigh and Sidgwick [24] introduced two modifications in the Clark cell that resulted in substantial improvements. They substituted zinc amalgam (percentage not stated) for zinc and used an H-shaped container in which the zinc anode could be kept entirely under solution and out of contact with the mercurous sulfate paste. Their design is illustrated by (c) in the figure. The zinc amalgam reduced the rate of gassing at the anode and by being under solution and out of contact with the mercurous sulfate paste the zinc anode exhibited more nearly constant potentials. Rayleigh and Sidgwick obtained 1.453 V for the absolute emf of their cells at 15 °C using a current balance (now known as a Rayleigh balance) and a B.A. resistor.

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Footnote 7: Rayleigh and Sidgwick prescribed these cells in June 1884. In the paper published in Dec. 1884 they added the note: "Some 4-cells have been set up Mr. Theophilus with amalgams of known composition, varying from 1/10 zinc to 1/10 zinc by weight. The duration of the test has as yet been scarcely adequate, but it appears that the smaller quantity of zinc is sufficient." In general, Clark cells were made, at a later date, with 7 to 10 percent amalgams.

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![Image](image-url)
These cells tended to leak in time, and Callendar and Barnes [67] recommended their hermetic sealing, (d) in figure 8. Other types of cell containers, also used for Weston cells, have been proposed and are illustrated in figure 8. Hulett [68] proposed a shorter cross-arm (e) and today some cells are made with no cross-arm but with a partition at the base of a single tube (f). Wright and Thompson [69] proposed the inverted-Y form, hermetically sealed, and Kahle [70] the same form but with a cork or ground-glass stopper (g); these are more difficult to fill. Cooper [71] proposed a modified Kahle type (h) which required no support in a thermostatically-controlled bath; his form could rest on a flat surface without support. The Cooper cell could also be used in water as well as in non-conducting oil because the cell terminals were not exposed but protruded above the bath fluid. Today, the H-shaped container, hermetically sealed, is used most widely; one single-tube type, either like (f) or in a modified form of the original design (a) are also made.

The reaction in the saturated Clark cell made with amalgamated anodes is:

$$n, y \text{Hg}(2p) + \text{Hg}_2\text{SO}_4(s) + \frac{7}{m} (\text{ZnSO}_4 + m \text{H}_2\text{O}(\text{sat} \text{aq}))$$

$$= \frac{m}{7} (\text{ZnSO}_4 + 7\text{H}_2\text{O}(c) + 2\text{Hg}(l) + (x-1)\text{Zn}, y \text{Hg}(2p)) \quad (5)$$

where $x$ = moles of Zn associated with $y$ moles of Hg in the amalgam, $2p = 2$-phase, and $m$ is the number of moles of water associated with 1 mole of $\text{ZnSO}_4$ in the saturated solution. Temporal amalgams are most commonly used; they are of two types, solid and liquid, with the solid phase being zinc (see fig. 9) [72]. The composition of the quid phase of a 10 percent zinc amalgam at various temperatures is given in column 2 of table 3.

The solubility of zinc sulfate in water changes considerably with temperature. Above 30 °C the soluble sulfate is $\text{ZnSO}_4 \cdot 6\text{H}_2\text{O}$; below 30 °C it is $\text{ZnSO}_4 \cdot 7\text{H}_2\text{O}$. The solubility of $\text{ZnSO}_4 \cdot 7\text{H}_2\text{O}$ in water from 0 to 30 °C is given in table 4. In saturated solution zinc sulfate hydrolyzes to give a solution containing 0.004 N sulfuric acid and having pH of 3.35 at 25 °C [73]. This concentration of acid is sufficient to prevent the hydrolysis of the mercurous sulfate used in the positive electrode (see ref. 1).

The emf of the Clark cell decreases as the temperature is increased; the decrease is about 0.1 percent per degree C. For the range 0 to 28 °C Illendorf and Barnes [67] gave, in volts:

$$E_t = E_{en} - 0.0032(t - 15 ^\circ) - 0.0000662(t - 15 ^\circ)^2 \quad (6)$$

The Clark cell has three advantages over the Weston cell, namely, (1) zinc sulfate hydrolyzes to produce sufficient sulfuric acid to prevent the hydrolysis of the mercurous sulfate paste; it, thereby, supplies its own buffering action, (2) the solid phase of the amalgam is a single component (zinc) whereas in the Weston cell the solid phase is a solid solution of cadmium and mercury; the emf of the Clark cell is less dependent, therefore, on the composition of the amalgam than is the Weston cell, and (3) the Clark cell shows less variation in temperature hysteresis than the Weston cell. However, the disadvantages of the Clark cell over the Weston cell well outweigh its advantages. These are: (1) The Clark cell tends to gas at the amalgam electrode. This gas as it forms slowly over the surface of the amalgam may dislodge crystals of $\text{ZnSO}_4 \cdot 7\text{H}_2\text{O}$ with adhering solution from the amalgam, and may eventually cause an open-circuit in the electric circuit unless $x$

![Figure 9. Phase diagram for the zinc-mercury system.](image)

<table>
<thead>
<tr>
<th>Temperature °C</th>
<th>Percentage of zinc</th>
<th>Percentage of cadmium</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>1.35</td>
<td>2.50</td>
</tr>
<tr>
<td>10</td>
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<td>6.40</td>
</tr>
<tr>
<td>40</td>
<td>2.90</td>
<td>7.80</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Temperature °C</th>
<th>ZnSO₄ in 100g H₂O</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>0.46 g</td>
</tr>
<tr>
<td>1</td>
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</tr>
<tr>
<td>2</td>
<td>0.44 g</td>
</tr>
<tr>
<td>3</td>
<td>0.43 g</td>
</tr>
<tr>
<td>4</td>
<td>0.42 g</td>
</tr>
<tr>
<td>5</td>
<td>0.41 g</td>
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<tr>
<td>6</td>
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<td>7</td>
<td>0.39 g</td>
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</tr>
<tr>
<td>10</td>
<td>0.36 g</td>
</tr>
<tr>
<td>11</td>
<td>0.35 g</td>
</tr>
<tr>
<td>12</td>
<td>0.34 g</td>
</tr>
<tr>
<td>13</td>
<td>0.33 g</td>
</tr>
<tr>
<td>14</td>
<td>0.32 g</td>
</tr>
<tr>
<td>15</td>
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</tr>
<tr>
<td>18</td>
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</tr>
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<td>19</td>
<td>0.27 g</td>
</tr>
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<td>0.26 g</td>
</tr>
<tr>
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</tr>
<tr>
<td>22</td>
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</tr>
<tr>
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<td>0.23 g</td>
</tr>
<tr>
<td>24</td>
<td>0.22 g</td>
</tr>
<tr>
<td>25</td>
<td>0.21 g</td>
</tr>
<tr>
<td>26</td>
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</tr>
<tr>
<td>27</td>
<td>0.19 g</td>
</tr>
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<td>30</td>
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</tr>
<tr>
<td>31</td>
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</tr>
<tr>
<td>32</td>
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</tr>
<tr>
<td>33</td>
<td>0.13 g</td>
</tr>
<tr>
<td>34</td>
<td>0.12 g</td>
</tr>
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<td>0.11 g</td>
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</tr>
<tr>
<td>37</td>
<td>0.09 g</td>
</tr>
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<td>38</td>
<td>0.08 g</td>
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<tr>
<td>39</td>
<td>0.07 g</td>
</tr>
<tr>
<td>40</td>
<td>0.06 g</td>
</tr>
</tbody>
</table>

* = transition temperature: $\text{ZnSO}_4 \cdot 7\text{H}_2\text{O} = \text{ZnSO}_4 \cdot 6\text{H}_2\text{O}$. 
on, as discussed later, is used in the con-
ne level of the crystals. (2) Zinc amalgam
oys with the platinum lead at the base of
the electrode. Since this alloy occupies
so than the platinum, strains are produced.
kage of the glass container follows. (3) The
k cell has an emf-temperature coefficient
about 30 times that of the Weston cell.
g to the relatively large change in the solu-
zinc sulfate with changes in temperature
of ZnSO₄·7H₂O tend to pass from the
c to the negative limb of the cell. During a
ure rise the volume of electrolyte over the
electrode becomes saturated more quickly.
t is usually a smaller volume than that over
the electrode. As a result a concentration
e between the limbs results and diffusion
lyte to the negative limb takes place until
centrarion difference is dissipated. This
can be prevented by making the vol-
e the negative and positive electrodes.
A similar phenomenon does not occur in
Weston cells because the change in solubility
of cadmium sulfate with temperature is much less
than that of zinc sulfate. (5) The Clark cell has
an emf which is considerably higher than unity
which, although not necessarily a disadvantage,
makes its use as a standard less convenient than a
Weston cell.
The emfs of saturated Clark cells are decreased
by addition of sulfuric acid to the electrolyte.
Some data based on measurements of Hulett [76]
are given in table 5.

<table>
<thead>
<tr>
<th>Normality of sulfate acid*</th>
<th>Change in emf</th>
</tr>
</thead>
<tbody>
<tr>
<td>Before saturation</td>
<td>After saturation</td>
</tr>
<tr>
<td>with ZnSO₄·7H₂O</td>
<td>with ZnSO₄·7H₂O</td>
</tr>
<tr>
<td>0.2024</td>
<td>0.1074</td>
</tr>
<tr>
<td>1.012</td>
<td>0.5466</td>
</tr>
<tr>
<td>2.024</td>
<td>1.1488</td>
</tr>
<tr>
<td></td>
<td>−0.00228</td>
</tr>
<tr>
<td></td>
<td>−0.00222</td>
</tr>
<tr>
<td></td>
<td>−0.00448</td>
</tr>
</tbody>
</table>

* = normality of acid in a saturated solution of pure zinc chloride at 25 °C is 0.004

5. The Weston (or Cadmium Sulfate) Cell

5.1. General

' Weston (or cadmium sulfate) cell is, for all
and purposes, the only electrochemical
sed today as a standard cell. Accordingly,
ns "standard cell" when used today in
median cadmium sulfate cells, and the re-
of this Monograph, appendices excepted,
this type of cell. The cell is made in
ral types, saturated and unsaturated where
ms refer to the state of the electrolyte.
ated type is the precision cell used in the
ance of the unit of emf. It may be man-
reproducible form and exhibits a con-
f for long periods of time. However, for
ision it must be maintained at a constant
ure owing to its relatively high emf-temp-
-figure. Most saturated cells must
ried, although some recent types have
le shippable by locking the electrodes
ith inert and porous septa. A
re less stable than the saturated type
r emf decreases slowly with time and is
as a reference of d-c voltage known within
ercent. It is usually made in a shippable
 septum over each electrode. It has
temperature stability and accordingly
est in ambient temperatures as an emf
ere 0.005 percent (0.05 mV) accuracy

saturated cell is also known as the Weston
Cell (or Element). It consists of a cadmium
pode and a mercury-mercurous sulfate
a saturated solution of cadmium sulfate
als of CdSO₄·8H₂O over the surface
odes. This cell may be represented
(2p)[CdSO₄·8H₂O(O)]CdSO₄(sat aq)]

CdSO₄·8/3 H₂O(c)Hg₂SO₄(s)Hg(0)(+)  

where the symbols have the same significance as
given above. The cell reaction is:

\[
x\text{Cd, } y\text{Hg(2p)} + \text{HgSO₄(s)} + \frac{8/3}{m-8/3} (\text{CdSO₄} \cdot m\text{H₂O}) \text{(sat aq)} 
\]

\[
= \frac{m}{m-8/3} (\text{CdSO₄} \cdot 8/3\text{H₂O})(c) + 2\text{Hg(l)} + (x-1)\text{Cd, } y\text{Hg(2p)} \]  

(7)

where \( x \) moles of Cd are associated with \( y \) moles of Hg in the amalgam and \( m \) is the number of moles of water associated with 1 mole of CdSO₄ in the saturated solution. At the end of the reaction the amalgam may be two phases (liquid and solid) or may be a liquid phase only, depending on the extent of the reaction and the relative amounts of amalgam and mercurous sulfate used in preparing the cell. When not discharged, as is normal when the cell is used as an emf standard, the amalgam remains in two phases. Cells are usually made with 10 or 12½ percent amalgams (see later).

The unsaturated cell differs from the saturated type only in that an unsaturated solution of cadmium sulfate and no crystals of CdSO₄·8/3H₂O are used. It is customary to use a solution that is saturated at 3 or 4 °C, the temperature range at which the salt exhibits a minimum solubility; the solution is then unsaturated at higher temperatures. The emf of the unsaturated cell at ambient room temperature is about 0.05 percent higher than that of the saturated type. The cell reaction is simply:

\[
x\text{Cd, } y\text{Hg(2p)} + \text{HgSO₄(s)} = \text{CdSO₄(aq)} 
\]

\[
+ 2\text{Hg(l)} + (x-1)\text{Cd, } y\text{Hg(2p)} \]  

(8)

unless the reaction is continued until crystals of CdSO₄·8/3H₂O are formed; then the reaction is the same as in the saturated cell. Again, when the cell is not discharged, as is normal when the cell is used as an emf standard, the solution remains unsaturated and the amalgam in two phases.
Both saturated and unsaturated standard cells are made as “neutral” or as “acid” cells; the saturated “neutral” type is also known as the Weston Normal Cell. These terms refer to the degree of acidity of the electrolyte with respect to sulfuric acid in the cell. If an aqueous solution of pure cadmium sulfate, to which no sulfuric acid is added, is used in the preparation of the cell, the cell is called a neutral type, even though the pH of a saturated aqueous solution of cadmium sulfate, owing to hydrolysis, is 4.00 at 25°C [73]. If sulfuric acid is added in sufficient amount to make the acidity 0.03 to 0.1 N, the cell is called an “acid” type. The purpose of adding the acid to the electrolyte is to prevent hydrolysis of the mercurous sulfate used in the cell; more details are given later. Today, most, if not all, cells are made of the “acid” type.

1.2. Preparation and Properties of Materials

The procedures employed at the National Bureau of Standards for the preparation and purification of materials for use in the construction of standard cells are described in the next few sections. In addition some properties of the materials, as they relate to standard cells, are given. Only four materials are required. These are mercury, cadmium, sulfuric acid, and water, all of which may be purified by distillation. To these four materials may be added a fifth, CdSO₄ · 8/3 H₂O, to avoid preparing from cadmium and sulfuric acid; it may be purified by repeated crystallizations from conductivity water.

Mercury of good grade, after washing in dilute acetic acid, then in distilled water, is dried and then distilled in a Hulet [77] still in a stream of dry air. In this method, the mercury is distilled near 200°C in a partial vacuum, air being drawn through the condenser at a rate to maintain the pressure at 25 mm, corresponding to an oxygen partial pressure of 5 mm. Any metallic vapor, except mercury, is oxidized and collects as a scum at the distillate which is removed by filtering through a fine pinhole in filter paper. Metals more soluble than mercury remain in the boiler of the still. Finally, the mercury is redistilled in a vacuum still. Procedures for purification of mercury of various grades are outlined in reference [76].

Cadmium of electrolytic grade is sublimed under reduced pressure. The sublimation is done at about 350 to 400°C in an evacuated Pyrex glass tube with an external electrical heating jacket. The distilled cadmium crystallizes out on the cooler parts of the tube but frequently adheres tightly to the glass walls. It is usually necessary to break the glass walls to remove the distilled cadmium adhering to the walls.

Sulfuric acid of reagent grade is twice distilled in all Pyrex still at a temperature of 270 to 290°C with the middle fraction being retained. Glass beads are placed in the boiler to reduce bumping and the distillation is carried out in a hood.

Water is repeatedly distilled in a Barnstead or comparable still until the conductivity of the water becomes as low or lower than 1 × 10⁻⁶ ohm⁻¹ cm⁻¹. This water is frequently called “conductivity water.”

Cadmium sulfate (CdSO₄ · 8/3 H₂O) of high grade is obtained by several recrystallizations of the C.P. salt. These recrystallizations are carried out from aqueous solutions below 43.6°C [79] since above this temperature the stable salt is the monohydrate, CdSO₄ · H₂O. Cadmium sulfate of high grade may also be prepared from pure cadmium and redistilled sulfuric acid solutions or from pure cadmium nitrate and redistilled sulfuric acid solutions, followed by recrystallizations of the salt from aqueous solutions in each case. The latter method is preferred rather than the use of very impure cadmium sulfate as starting material.

Both hydrates, CdSO₄ · 8/3 H₂O and CdSO₄ · H₂O, are highly soluble in water; the solubility of the former increases with temperature while that of the latter decreases. The solubilities of each as a function of temperature are given in table 6 [79, 80, 81]. The solubilities are expressed as the number of grams of the anhydrous salt in 1000 g of water.

Saturated solutions of CdSO₄ · 8/3 H₂O begin to freeze at -17°C and become completely frozen at -24°C; these temperatures, then, represent the lower limit for the use of cadmium sulfate cells (see later). It has been reported [82] that CdSO₄ · 8/3 H₂O shows a transition to CdSO₄ · 7H₂O at 4°C. However, cells tested in this temperature range do not exhibit an abrupt inflection in emf at 4°C indicative of a phase change but a smooth maximum in the range of 3 to 4°C indicative of a minimum solubility in cadmium sulfate (see table 6).

The amalgam may be prepared either electrolytically by depositing cadmium in mercury or by heating the two metals together. In the former, crystals of purified CdSO₄ · 8/3 H₂O are placed on the surface of mercury (contained on the bottom of a beaker) and covered with distilled water acidified with a few drops of sulfuric acid. Mercury is made

<table>
<thead>
<tr>
<th>Temperature, °C</th>
<th>CdSO₄ · 8/3 H₂O (as CdSO₄)</th>
<th>CdSO₄ · H₂O (as CdSO₄)</th>
</tr>
</thead>
<tbody>
<tr>
<td>-18</td>
<td>767.6</td>
<td></td>
</tr>
<tr>
<td>-15</td>
<td>766.4</td>
<td></td>
</tr>
<tr>
<td>-10</td>
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<td></td>
</tr>
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</tr>
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</tr>
<tr>
<td>72</td>
<td>700.0</td>
<td></td>
</tr>
</tbody>
</table>

*—transition temperature.
mode and a platinum foil suspended in the solution at the top serves as anode. Usually, the amount of \( \text{CdSO}_4 \cdot \frac{8}{3} \text{H}_2\text{O} \) needed to form an amalgam with the desired percentage of cadmium is used. Since the crystals dissolve in a current of low magnitude is used initially, nearly all the cadmium is deposited. The beaker is then increased to about 5 times the initial or 30 minutes, and then, with the current running, washing with distilled water is started. Residue is successively added and decanted until the volume decreases to less than 0.01 A for an im.

A cadmium rod may be used as anode in native procedure; the amount of cadmium and in the mercury is determined from the and time by Faraday's law.

method in which the two metals are heated is more convenient. The propensities of metals are melted together in a covered casserole, in a hood, until completely and homogeneous. A slight scum may rise to the surface. This is brushed aside and air. Amalgam immediately transferred to an irrotating covered buret and introduced to the cell through an electrically heated tube. Any small amount of scum on the top of the amalgam will disappear as soon as cadmium sulfate is added to the cell. The top method now used at the National Bureau of Standards.

difference in the properties of standard cells using amalgams prepared by these methods is observed. Amalgams exhibit less erratic behavior and correlation rapidly, if at all, than pure unamalgamated amalgams when in contact with aqueous solutions of salts. Amalgamation raises the hydrogen tage of metals and reduces stresses within the cell. It is for these reasons that amalgams better anodes for standard cells than the metals. A 10 or 12½ percent amalgam is usually used commercially in constructing cadmium sulfate cells. A 10 percent amalgam is now the National Bureau of Standards. These eight percentages at normal temperatures of these percentages consist of two, a liquid and a solid phase. The solid phase lid solution of cadmium and mercury. The diagram [83] for the cadmium-mercury system is given in figure 10. The composition of the phase of a 10 percent amalgam is listed for temperatures in column 3 of table 3.

Mercuroful sulfate may be prepared in a number of ways as follows:

1. By the reaction between sulfuric acid and mercuric nitrate [84].
2. By the action of fuming sulfuric acid on mercury [64].
3. By the action of dilute nitric acid in sulfuric acid on mercury [44, 84].
4. By the reduction of mercuric sulfate by mercury [44].
5. By the reduction of mercuric sulfate by sulfuric acid [44].
6. By the reduction of mercuric sulfate by formaldehyde [85].
7. By the recrystallization of commercial mercuric sulfate from sulfuric acid [84].
8. By c-c electrolysis [86].
9. By d-c electrolysis [44, 68].

Of these methods standardization has been on the last one which is now used by the National Bureau of Standards. By d-c electrolysis uniform samples of mercuric sulfate of high purity and reproducible grain size are obtained. Such samples are free of all foreign materials except sulfuric acid, water, and mercury, all of which are used in standard cells, and especially in the mercuric sulfate paste. In this method [44, 60] mercaptan anodes, platinum cathodes, and a 1:6 sulfuric acid-water solution are used and electrolysis is carried out in a darkened room (see sec. 7.7). Mercury is placed on the bottom of one or two shallow glass vessels. These vessels are then placed on a glass stand one above the other, as shown in figure 11, in a deeper and larger dish ½ filled with the sulfuric acid solution; the acid solution extends over the shallow vessels. The upper dish contains a central glass tube through which passes the shaft for the stirrer for the lower dish; obviously this is unnecessary if only one shallow dish was used. A platinum-foil cathode is placed near the top of the solution. The solution is vigorously stirred at 70 to 200 rpm and

![Figure 10. Phase diagram for the cadmium-mercury system.](image-url)
current density at the mercury surface is maintained at 1 to 2 A per 100 cm². When the electrolyte becomes saturated with mercurous sulfate the iodid salt appears on the surface of the mercury and must be swept off into the outer dish by stirring in order to keep the surface of the mercury electrode clean. In this stirring finely divided mercury comes mixed with the mercurous sulfate to give gray product. Electrolysis is continued until the cleared amount of gray mercurous sulfate has been pared; the current is then cut off but stirring is continued for several hours. Photographs of the electrolytic production of mercurous sulfate are shown in figure 11.

For “neutral” cells the mercurous sulfate is then shed repeatedly with a saturated solution ofinium sulfate and then stored under such a solution until used. For “acid” cells the mercurous sulfate is stored under the electrolysis solution until needed at which time it is washed thoroughly with the solution of the type to be used in the cells. Mercurous sulfate is the oxidizing agent or the depolarizer” used in Weston cells. It is highly soluble in water and in dilute solutions of sulfuric acid. The solubility of mercurous sulfate, expressed in terms of mercury, in various concentrations of sulfuric acid is listed in table 7 at 0 and 25°C [87]. In aqueous solutions mercurous sulfate drolizes according to the reaction:

\[ \text{gsSO}_4(s) + \text{H}_2\text{O}(l) = \text{Hg}_2\text{O} \cdot \text{Hg}_2\text{SO}_4(s) + \text{H}_2\text{SO}_4(aq) \] (9)

showed that it did not change appreciably with temperature, being 0.00198 N at 0°C and 0.00216 N at 28°C. Although, theoretically, a concentration slightly exceeding the equilibrium concentration could be used to prevent the hydrolysis of mercurous sulfate, a higher concentration is recommended. In initial studies [90], solutions 0.03 N to 0.05 N with respect to sulfuric acid were used, in part because mercurous sulfate exhibits a minimum solubility in the range from 0.04 to 0.08 N. (Hulett [91] and Sir Frank Smith [92] found the minimum solubility of mercurous sulfate to be at approximately 0.04 N, while Craig, Vinal, and Vinal found it to be at 0.06 N at 28°C and 0.08 N at 0°C.) Now, the lower acidity value is preferred since cells with the lower acidity have shown the greater stability in emf. Cells with 0.1 N acid, for example, tend to gas as a result of the action of the acid with the cadmium amalgam.

Concentrations of sulfuric acid somewhat higher than the equilibrium value are chosen, not only because of the decrease in the solubility of mercurous sulfate in aqueous solutions of sulfuric acid.
sulfate but because the acid decreases the solubility of the glass container by the elec-
tric field. It is well known that glasses are more resistant to neutral salt or alkaline solutions than to acids [93, 94]. The final solution is titrated with sodium hydroxide using methyl purple as an indicator, which has a pH transformation interval of 3.4 [95].

3. Containers for Standard Cells

Standard cells as made at the National Bureau of Standards are of the H-form shown in Fig. 12. Photographs of a cell container and a completed cell constitute Figure 13. The container of Kimble Standard Flint glass, a chemically resistant soda-lime glass, having an average thermal expansion coefficient of \(92 \times 10^{-7}\) per degree C. (The coefficient of linear thermal expansion is the increase in length per unit length, and at 0°C per degree Celsius.) Since this thermal expansion coefficient approximates platinum, \(80 \times 10^{-7}\) per degree C, vacuums are obtained at the platinum leads. Platinum-containing sealing-in glass is used in the platinum leads at the bottom of each cell, which will prevent the lead leading deterioration. On the average the height of the cell is about 92 mm, the diameter of the vessel about 16 mm, the diameter of the cross section 11 mm, and the distance between limbs 2 mm. A constriction is made near the bottom limbs, as shown, to lock in part of the cell's mixture of \(\text{CdSO}_4 \cdot 8/3\text{H}_2\text{O}\). The constriction is complete circumferential indentation or consists of several knobs directed inward. Constrictions are placed so that crystals of \(\text{CdSO}_4 \cdot 8/3\text{H}_2\text{O}\) are both below and above them. Locked crystals prevent the displacement of materials in the cell limbs, and those at the seal prevents an opening of the circuit within by any gas that might form on the amalgam. Platinum leads are secured by cotton thread in clockwork fashion around each limb at the constrictions and ed in place by collodion; platinum leads tendency to break mechanically at the glass not securely held in place. For permanent bonding, a number of threads are stitched on each cell on the wall of the container with hydrofluoric acid. Filling with cell constituents the container is washed with nitric acid, rinsed with water, steamed, and then dried at 110°C. Various times attempts have been made to pyrex cell containers. Fused silica, however, has two major drawbacks. It has such a low linear thermal expansion coefficient \((5 \times 10^{-7}\) per degree C) that the electrical leads have to be brought into the cell in a special way. Also, a very high temperature must be employed to seal the cell; the chemicals within the cell may thereby be affected. These two drawbacks have been solved by the cell design [96] shown in figure 14. The main features of this design are (1) the use of two seals at each arm and (2) a graded seal between the fused silica and Pyrex at the top of each limb of the container. The use of the graded seals makes possible the sealing of the cell at a low temperature after filling. Transparent silica is used to facilitate the filling of the cells. The two seals at each arm are spaced about 7 cm
withdrawn from the cell without any of the material touching the container walls.

Mercury is first placed in the bottom of one limb and the amalgam in the bottom of the other limb, each to a depth of about 6 mm. The amalgam is added while warm and in a single liquid phase; on cooling the amalgam becomes two-phased, solid and liquid. The mercurous sulfate is then placed in a Gooch or similar crucible, washed free of the solution under which it was stored with dilute sulfuric acid and then washed with solution of the type to be used in the cell, and then while moist introduced over the mercury to a depth of about 12 mm. The mercurous sulfate should be mixed with a small amount of mercury (partially done during the electrolytic preparation of mercurous sulfate) and finely divided crystals (fineness of granulate sugar) of CdSO$_4$·8H$_2$O prior to introduction to the cell; this mixing may be done prior to the washing procedure. The mixing and washing of the mercurous sulfate paste hastens the attainment of chemical equilibrium within the cell after its assembly.

Crystals of CdSO$_4$·8H$_2$O, of a size that pass through a tube of 4-mm bore, are then added to both limbs of the cell to a depth of about 10 mm at the negative electrode and about 8 mm at the positive electrode. Finally, a saturated solution of CdSO$_4$·8H$_2$O is added to a level slightly above the crossarm, and the cell is then hermetically sealed.

In some cells, especially of larger size, large crystals (about 10 to 15 mm in diameter) of CdSO$_4$·8H$_2$O are used. Larger crystals have an advantage; new smaller crystals that may form at the electrode surface (especially the negative one) will not become entrapped by the crystals whereby an open circuit might be produced. However, cells with large crystals tend to come to equilibrium, after a temperature change, more slowly than those made with small crystals.

Unsaturated cells are made similarly except that no crystals of CdSO$_4$·8H$_2$O are used and the are made portable (shippable) by inserting corr or plastic rings, covered with linen, over the electrode surfaces. In some cells ceramic discs, either locked in place or supported by ceramic rod which protrudes through stoppers in each limb, are used [99,100]. The unsaturated cell is the commercial type used widely in the United States for work requiring no greater accuracy than ±0.005 percent; it is not made at the National Bureau of Standards. It is used for pyrometer work, in pH meters, recording instruments, etc., and is usually housed in nontransparent copper-shielded cases for general laboratory work. A copper-shielded case is employed to assure a uniform temperature at both limbs of the cell (see later). Saturated cells are not mounted in cases since they are intended for immersion in temperature-controlled oil baths. Commercial saturated cells are usually mounted in groups of 3, 4, or 6 on special racks.
nience in use. NBS saturated cells are in oil as described above in section 2.3.

The cells are encased in a constant temperature in thermostatted oil baths or in portable thermo-controlled air boxes. The latter are made after a design first proposed by ND Stimson [101]. The cells are housed in a metal box which rests in a larger aluminum box, the temperature of which is controlled by a mercury-in-glass thermometer.

The aluminum boxes are thermally insulated and enclosed in a wooden box which contains an a-c relay, a transformer, and a timer. The box is operated on 110 V 60-cycle power.

The leads from the individual cells are attached to binding posts on the outside of the box. These are designed to operate at room temperature; the choice of tempepdent on the location where the box is made or on the size of the box. A rule of thumb used as a temperature of 70°C is used. The temperature of the cells in the box is measured by a mercury-in-glass thermometer provided with the box. In some cases, a well is added to provide for a platinum-platinum electrode in which the temperature is measured. A detailed description of a timeon box is given in Appendix 7.

Electromotive Forces of Newly Made Cells

When first made, cells exhibit emfs that will differ considerably from the expected values. Values steady at 10 µV or 0.1 µV are usually obtained within a few minutes, but the cells may be required to reach steady to 0.1 µV are attained. In some cases, the emfs decline in their approach to the expected values, in other cases they increase.

There are two reasons for this “aging” process. One is the process of equilibration, in which acid sulfate paste is allowed to reach equilibrium within the cell. This is readily seen during the filling process, and since the preparation of cadmium sulfate paste is a slow process, the cells must be aged for at least a week. If this process is continued for a longer period, it may be possible to improve the cells. The other reason is the reaction of the amalgam and the glass container.

However, this reaction eventually ceases when the emf stability of cells which have been “aged” (see later). If reproducibility of 0.01 mV in emf is considered adequate, the cell is ready for use.

Cells within any one group, although made at the same time, may differ both initially but may persist for years; i.e., individual cells, although differing in emf may show high stability in emf. Although diffusion is a slow process, acid or solution concentration inequalities within any one cell cannot explain these differences. Instead they must arise from slight differences in the composition or the amalgam between cells, or as it is called, the horizontal sections; this figure is discussed in sec. 6.3) even though precautions are taken to keep the amalgam homogeneous during the filling process. (2) from slight differences in the acidity of the solutions between cells produced during the filling process or in interactions with the glass containers, and/or (3) to slight differences between cells in the grain size of the mercurosulfate used in the positive electrodes.

Figure 15. Relation of the electromotive force of the cadmium sulfate standard cell to the percentage of cadmium in the amalgam and the temperature.

6.1. Concentration of Solution

The emf of cadmium sulfate cells depends on the concentration of the cadmium sulfate solution. Over a limited range of concentration near saturation the emf increases about 0.0017 V for a one percent decrease in cadmium sulfate content. For more dilute solutions the change is somewhat greater. In table 8 the emfs at 25 °C corresponding to various concentrations of cadmium sulfate, near saturation, are given. These data are based on results of Vosburgh and Eppley [102] for cells containing 12 1/2 percent amalgams and 0.023 N H₂SO₄; their data reported in international volts have been converted to absolute volts here. For neutral solutions the emfs listed here would be 18 μV higher.

Table 8. Electromotive forces of cadmium sulfate cells at 25 °C as a function of electrolyte concentration

<table>
<thead>
<tr>
<th>CdSO₄</th>
<th>Enf</th>
<th>CdSO₄</th>
<th>Enf</th>
</tr>
</thead>
<tbody>
<tr>
<td>41.84</td>
<td>1.01219</td>
<td>42.98</td>
<td>1.01899</td>
</tr>
<tr>
<td>42.39</td>
<td>1.0097</td>
<td>43.06</td>
<td>1.01899</td>
</tr>
<tr>
<td>42.63</td>
<td>1.00973</td>
<td>43.12</td>
<td>1.018794</td>
</tr>
<tr>
<td>42.77</td>
<td>1.010315</td>
<td>43.22</td>
<td>1.018603</td>
</tr>
<tr>
<td>42.99</td>
<td>1.010321</td>
<td>43.405</td>
<td>1.018392</td>
</tr>
</tbody>
</table>

*—saturated solution.

6.2. Acidity of Solution

The addition of sulfuric acid slightly decreases the emf of a cadmium sulfate cell. For the saturated cell several equations have been proposed relating the change in emf to acid concentration. For acid concentrations up to 4 N Sir Frank Smith [103] gave:

\[ \Delta E (\text{volts}) = -(0.00060x + 0.00005x^2) \]  
(10)

where \( \Delta E \) is the difference in emf of acid cells from neutral ones and \( x \) is the normality of the sulfuric acid solution before it is saturated with CdSO₄·8/3 H₂O. For acid concentrations up to 0.4 N only, the National Physical Laboratory [104] gave the linear relation

\[ \Delta E (\text{microvolts}) = -615x. \]  
(11)

Obata [105] and Ishibashi and Ishizaki [106] also gave linear relations with the coefficients being, respectively, -855 and -833: Vosburgh [107] found Obata’s equation to be valid to 1.49 N. In these last two, \( x \) refers to the normality of the acid in a saturated solution of CdSO₄·8/3 H₂O. All of these formulas agree closely if applied properly. For low acidities, the acidity of a solution of sulfuric acid after saturation with CdSO₄·8/3 H₂O is 0.76% of that before saturation.

Differences between the emf of “neutral” and “acid” cells according to the Smith formula are listed in table 9. Sir Frank Smith [103] investigated the effect on the emf of cadmium sulfate cells if the acid were confined to one or the other of the electrode compartments. For the effects, valid to 4 N, he gave:

\[ \Delta E_{\text{negative}} (\text{volts}) = 0.01090x - 0.00125x^2 \]  
\[ \Delta E_{\text{positive}} (\text{volts}) = -0.01150x + 0.0012x^2 \]  
(12)

the summation of which gives the Smith equation above for the effect of acid on the emf of the cell as a whole. These differences for various normalities of acid are given in table 10. These relations show that more acid at the negative electrode increases the emf while more acid at the positive electrode produces a decrease in emf. It is necessary, then, for high reproducibility and stability of emf that the acidity be the same and remain the same at the two electrodes.

Table 9. Differences of emf of “acid” cells from the standard value of Weston “neutral” cells

<table>
<thead>
<tr>
<th>Normality of H₂SO₄</th>
<th>Difference of emf</th>
<th>Normality of H₂SO₄</th>
<th>Difference of emf</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.01</td>
<td>-1.6</td>
<td>0.30</td>
<td>-1.85</td>
</tr>
<tr>
<td>0.02</td>
<td>-1.8</td>
<td>0.40</td>
<td>-2.48</td>
</tr>
<tr>
<td>0.03</td>
<td>-2.0</td>
<td>0.50</td>
<td>-3.12</td>
</tr>
<tr>
<td>0.04</td>
<td>-2.4</td>
<td>0.60</td>
<td>-3.78</td>
</tr>
<tr>
<td>0.05</td>
<td>-3.0</td>
<td>0.70</td>
<td>-4.44</td>
</tr>
<tr>
<td>0.06</td>
<td>-3.9</td>
<td>0.80</td>
<td>-5.12</td>
</tr>
<tr>
<td>0.07</td>
<td>-4.8</td>
<td>0.90</td>
<td>-5.80</td>
</tr>
<tr>
<td>0.08</td>
<td>-5.8</td>
<td>1.00</td>
<td>-6.50</td>
</tr>
<tr>
<td>0.09</td>
<td>-5.4</td>
<td>2.00</td>
<td>-1.40</td>
</tr>
<tr>
<td>0.10</td>
<td>-6.0</td>
<td>3.00</td>
<td>-3.20</td>
</tr>
<tr>
<td>0.20</td>
<td>-122</td>
<td>4.00</td>
<td>-5.00</td>
</tr>
</tbody>
</table>

Table 10. Differences of emf of cells from the standard value of Weston “neutral” cells if the acid is confined to the negative or positive limb of cell

<table>
<thead>
<tr>
<th>Normality of H₂SO₄</th>
<th>Differences of emf, microvolts</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Negative limb</td>
</tr>
<tr>
<td>0.01</td>
<td>+109</td>
</tr>
<tr>
<td>0.03</td>
<td>+218</td>
</tr>
<tr>
<td>0.05</td>
<td>+338</td>
</tr>
<tr>
<td>0.06</td>
<td>+542</td>
</tr>
<tr>
<td>0.07</td>
<td>+650</td>
</tr>
<tr>
<td>0.08</td>
<td>+757</td>
</tr>
<tr>
<td>0.10</td>
<td>+864</td>
</tr>
<tr>
<td>0.20</td>
<td>+1078</td>
</tr>
<tr>
<td>0.30</td>
<td>+2310</td>
</tr>
<tr>
<td>0.40</td>
<td>+3157</td>
</tr>
<tr>
<td>0.50</td>
<td>+4160</td>
</tr>
<tr>
<td>0.60</td>
<td>+5138</td>
</tr>
<tr>
<td>0.70</td>
<td>+6090</td>
</tr>
<tr>
<td>0.80</td>
<td>+7018</td>
</tr>
<tr>
<td>0.90</td>
<td>+8798</td>
</tr>
<tr>
<td>1.00</td>
<td>+9560</td>
</tr>
<tr>
<td>1.00</td>
<td>+10302</td>
</tr>
<tr>
<td>1.00</td>
<td>+11060</td>
</tr>
<tr>
<td>1.00</td>
<td>+12040</td>
</tr>
</tbody>
</table>
Composition of the Amalgam

The composition of the amalgam as may be seen by the curves plotted in figure 15. This figure shows that the useful range of amalgam composes from about 8 to 14 percent cadmium for temperatures. The useful range of amalgam for standard cells is limited to the part of the curves, here the emf is very low and not critically dependent on the percentage of cadmium in the amalgam. In the amalgam consists of two phases, liquid, with the solid phase being a solid of mercury and cadmium. For low and moderate percentages of cadmium the emf is very sensitive to one exact amount of cadmium in the amalgam sensitivity is more marked at lower temperatures.

In figure 16 is shown the range over which various amalgams can be used for a 12 1/2% per cent of amalgam is about 12 to 62 °C, while for a 10% amalgam the range is from about 8 to 14 °C for this reason a 10 percent is used in cells made at the National Standards. The significances of the red lines A and B appearing in figure 16 is some under the section on cadmium the significance of the upper dotted line is in the next section.

Crystal Phases of Cadmium Sulfate

stated above, cadmium sulfate over a temperature range exists in two different forms CdSO₄ · 8H₂O and CdSO₄ · 9H₂O with the temperature being 43.6 °C, below which the hydrate is the stable form. The emfs of standard cells made with these two hydrates differ except at the transition where the emfs are the same. Cells can be made to have the same range for short periods of time. Each cell at a particular temperature with the more stable hydrate have the same emf. These facts are illustrated by the data in table 11. These cells were “neutral” with 10 percent amalgams. When a cell particular hydrate is carried over into an able range its emf will correspond at first a supersaturated solution of the metastable and then slowly rise in value as the hydrate is converted to the more stable form. This transition in phase is slow unless the two hydrates are present; then the transition is relatively fast. Accordingly, overheating of normal cells may have only transient adverse effects if the overheating is only momentary; otherwise the adverse effects may persist for long periods of time. In any case normal type saturated cells made with crystals of CdSO₄·8/3 H₂O should not be heated above 43.6 °C; the upper dotted line in figure 16 corresponds to this upper temperature limit.

Table 11. The emfs of Weston Normal Cells made with crystals of CdSO₄·8/3 H₂O or crystals of CdSO₄·9H₂O

<table>
<thead>
<tr>
<th>Temperature (°C)</th>
<th>CdSO₄·8/3 H₂O Cells</th>
<th>CdSO₄·9H₂O Cells</th>
</tr>
</thead>
<tbody>
<tr>
<td>20</td>
<td>1.01866</td>
<td>1.01331</td>
</tr>
<tr>
<td>25</td>
<td>1.01844</td>
<td>1.01417</td>
</tr>
<tr>
<td>30</td>
<td>1.01817</td>
<td>1.01561</td>
</tr>
<tr>
<td>35</td>
<td>1.01785</td>
<td>1.01587</td>
</tr>
<tr>
<td>40</td>
<td>1.01756</td>
<td>1.01519</td>
</tr>
<tr>
<td>43.4**</td>
<td>1.01729</td>
<td>1.01729</td>
</tr>
<tr>
<td>45</td>
<td>1.01716</td>
<td>1.01737</td>
</tr>
<tr>
<td>50</td>
<td>1.01682</td>
<td>1.01842</td>
</tr>
</tbody>
</table>

*Original data of ref. (149) were in international units, are converted here to standard volts. **A better value for the transition temperature in 43.6 °C (79).

7. Characteristics of Standard Cells

Emf-Temperature Coefficient

Standard cells have a very low emf-temperature coefficient. Although it is frequently unsaturated standard cells have a dE/dt of 1 V/deg C, the emf-temperature coefficient of temperature, is dependent on the concentration of the electrolyte, and increases as the cell ages. In table 12, values of dE/dt are given for temperatures from 15 °C to 45 °C for various weight percents of CdSO₄. The emf values corresponding to cells made with the various concentrations of CdSO₄ are given at 25 °C as an aid to users in determining the emf-temperature coefficient of a particular cell. For example, if a cell had at 25 °C an emf of 1.019043 V its dE/dt would be
Table 12. Emf-temperature coefficients of unsaturated standard cells
(In microvolts per degree Celsius)

<table>
<thead>
<tr>
<th>CASO₄</th>
<th>Emf, 25°C</th>
<th>15°C</th>
<th>20°C</th>
<th>25°C</th>
<th>30°C</th>
<th>35°C</th>
<th>40°C</th>
<th>45°C</th>
</tr>
</thead>
<tbody>
<tr>
<td>41.84</td>
<td>1.011289</td>
<td>-12.9</td>
<td>-13.2</td>
<td>-13.5</td>
<td>-12.9</td>
<td>-11.5</td>
<td>-9.2</td>
<td>-6.1</td>
</tr>
<tr>
<td>41.69</td>
<td>1.011269</td>
<td>-5.7</td>
<td>-5.9</td>
<td>-5.7</td>
<td>-5.7</td>
<td>-5.3</td>
<td>-4.6</td>
<td>-3.9</td>
</tr>
<tr>
<td>41.77</td>
<td>1.011257</td>
<td>-1.2</td>
<td>-1.3</td>
<td>-1.3</td>
<td>-1.2</td>
<td>-1.1</td>
<td>-1.0</td>
<td>-1.0</td>
</tr>
<tr>
<td>42.00</td>
<td>1.011221</td>
<td>+1.6</td>
<td>+1.6</td>
<td>+1.7</td>
<td>+1.7</td>
<td>+1.7</td>
<td>+1.7</td>
<td>+1.7</td>
</tr>
<tr>
<td>42.94</td>
<td>1.010943</td>
<td>+2.0</td>
<td>+2.0</td>
<td>+2.0</td>
<td>+2.0</td>
<td>+2.0</td>
<td>+2.0</td>
<td>+2.0</td>
</tr>
<tr>
<td>43.20</td>
<td>1.010969</td>
<td>+2.2</td>
<td>+2.2</td>
<td>+2.2</td>
<td>+2.2</td>
<td>+2.2</td>
<td>+2.2</td>
<td>+2.2</td>
</tr>
<tr>
<td>43.03</td>
<td>1.010986</td>
<td>+3.0</td>
<td>+3.0</td>
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<td>+3.0</td>
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<td>+3.0</td>
<td>+3.0</td>
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<tr>
<td>43.12</td>
<td>1.010904</td>
<td>+3.8</td>
<td>+3.8</td>
<td>+3.8</td>
<td>+3.8</td>
<td>+3.8</td>
<td>+3.8</td>
<td>+3.8</td>
</tr>
<tr>
<td>43.22</td>
<td>1.010930</td>
<td>+4.6</td>
<td>+4.6</td>
<td>+4.6</td>
<td>+4.6</td>
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<tr>
<td>43.40</td>
<td>1.010892</td>
<td>+5.4</td>
<td>+5.4</td>
<td>+5.4</td>
<td>+5.4</td>
<td>+5.4</td>
<td>+5.4</td>
<td>+5.4</td>
</tr>
</tbody>
</table>

- This composition corresponds to a solution saturated at 4°C and gives a cell with a dead of zero at 25°C.
- 10% of the solutions saturated with CASO₄ = 3% H₂SO₄ at the respective temperatures.
- Contains 0.03 N H₂SO₄.

-0.4 μV/deg C at 25°C, while if it had an emf of 1.018704 V its dE/dt would be +1.3 μV/deg C. Inspection of the data of table 12 also shows that a cell made with a solution containing 42.98 wt percent of CASO₄ has a zero emf-temperature coefficient at 25°C. Vosburgh and Eppley [102] showed that this percentage corresponds closely to a solution saturated at 4°C (the solutions of Vosburgh and Eppley also contained 0.023 N H₂SO₄). Since a solution saturated in the range of 3°C to 4°C leads to cells with negligible emf-temperature coefficients such solutions are frequently used in the construction of unsaturated standard cells.

Saturated standard cells exhibit a much larger emf-temperature coefficient than unsaturated standard cells owing to the change in solubility of CASO₄ - 3H₂O with temperature. They exhibit a maximum emf at 3°C to 4°C, the temperature range of the minimum solubility of CASO₄ - 3H₂O (see table 6). Two formulas relating the emf and temperature have been proposed. Wolff [32] working with 12½ percent amalgams obtained:

\[ E(t) = E_{20} + 0.000004060(t - 20) - 0.00000000950(t - 20)^2 + 0.0000000001(t - 20)^3 \]  (14)

in international volts where \( E \) is the emf at temperature \( t \) and \( E_{20} \) is the emf at 20°C. This equation is known as the International Temperature Formula. It is valid from 12°C to 90°C but may be used to 0°C as long as the liquid and solid phases of the amalgam are present. Vigneur and Watts [110] using 6 and 10 percent amalgams, to extend the temperature range, obtained:

\[ E(t) = E_{20} - 0.0000003939(t - 20) - 0.00000000930(t - 20)^2 + 0.0000000006600(t - 20)^3 - 0.0000000000150(t - 20)^4 \]  (15)

in international volts. These two equations are also applicable in absolute volts. This later equation is valid from -20 to 40°C; Vignon and Watts used the 6 percent amalgam for the lower temperature but the 10 percent amalgam gives the same result as long as the amalgam contains liquid and solid phases; thereafter the emf decreases below that given by eq (15). The cell becomes completely frozen at -24°C, eq (15) gives -1139.5 μV for \( E_{24} \), i.e., \( E_{20} \). However, when the cell becomes completely frozen the emf is approximately 1.007 V.

The emf of "neutral" saturated standard cells, a function of temperature, based on the above formulas, is given in figure 17. Both formula reproduce the maximum in emf at 3°C to 4°C, the temperature range of the minimum solubility of CASO₄ - 3H₂O. Since the acidity of the electrolyte does not appreciably affect \( dE/dt \), the emf of "acid" cells would parallel the curve shown. The displacements in the curves would depend on the acidity employed (see sec. 6.2). In this figure the value at 20°C, the temperature at which international comparisons are made, is labeled Emf standard.

The differences between eq (14) and (15) are not large. In table 13 the differences in emf at various temperatures from the emf at 20°C as given by these two formulas are given. Since 10 percent amalgams are now used widely in preparing saturated standard cells eq (15) (or 16 below) should be used to calculate the change in their emf with temperature.

Above 43.6°C where CASO₄ - 3H₂O transforms to CASO₄ - H₂O the emf-temperature relation is given by [109]:

\[ E(t) = E_{43.6} + 0.000173(t - 43.6) \]  (16)

Figure 17. Relation of the electromotive force of the cadmium sulfate standard cell to the temperature.
Differences in emf of saturated standard cells from the value at 20°C

<table>
<thead>
<tr>
<th>Temperature</th>
<th>Vigueux and Watts formula</th>
<th>International formula</th>
</tr>
</thead>
<tbody>
<tr>
<td>°C</td>
<td>volts</td>
<td>volts</td>
</tr>
<tr>
<td>575.44°</td>
<td>13</td>
<td>229.0</td>
</tr>
<tr>
<td>575.45°</td>
<td>14</td>
<td>202.3</td>
</tr>
<tr>
<td>482.09°</td>
<td>15</td>
<td>73.3</td>
</tr>
<tr>
<td>494.40°</td>
<td>16</td>
<td>62.7</td>
</tr>
<tr>
<td>312.17°</td>
<td>17</td>
<td>109.9</td>
</tr>
<tr>
<td>253.69°</td>
<td>18</td>
<td>75.2</td>
</tr>
<tr>
<td>264.08°</td>
<td>19</td>
<td>38.7</td>
</tr>
<tr>
<td>-98.6°</td>
<td>20</td>
<td>0.0</td>
</tr>
<tr>
<td>-37.9°</td>
<td>21</td>
<td>-0.3</td>
</tr>
<tr>
<td>218.7°</td>
<td>22</td>
<td>-82.2</td>
</tr>
<tr>
<td>69.3°</td>
<td>23</td>
<td>-126.1</td>
</tr>
<tr>
<td>152.8°</td>
<td>24</td>
<td>-171.4</td>
</tr>
<tr>
<td>157.9°</td>
<td>25</td>
<td>-218.8</td>
</tr>
<tr>
<td>195.6°</td>
<td>26</td>
<td>-267.7</td>
</tr>
<tr>
<td>229.2°</td>
<td>27</td>
<td>-316.1</td>
</tr>
<tr>
<td>258.7°</td>
<td>28</td>
<td>-370.2</td>
</tr>
<tr>
<td>284.3°</td>
<td>29</td>
<td>-425.9</td>
</tr>
<tr>
<td>309.3°</td>
<td>30</td>
<td>-479.2</td>
</tr>
<tr>
<td>338.0°</td>
<td>31</td>
<td>-536.1</td>
</tr>
<tr>
<td>338.7°</td>
<td>32</td>
<td>-594.6</td>
</tr>
<tr>
<td>350.9°</td>
<td>33</td>
<td>-654.6</td>
</tr>
<tr>
<td>350.9°</td>
<td>34</td>
<td>-710.0</td>
</tr>
<tr>
<td>364.2°</td>
<td>35</td>
<td>-779.6</td>
</tr>
<tr>
<td>363.6°</td>
<td>36</td>
<td>-844.4</td>
</tr>
<tr>
<td>363.4°</td>
<td>37</td>
<td>-911.0</td>
</tr>
<tr>
<td>358.8°</td>
<td>38</td>
<td>-979.1</td>
</tr>
<tr>
<td>350.8°</td>
<td>39</td>
<td>-1049.0</td>
</tr>
<tr>
<td>340.5°</td>
<td>40</td>
<td>-1120.6</td>
</tr>
<tr>
<td>328.3°</td>
<td>41</td>
<td>(-1193.8)</td>
</tr>
<tr>
<td>313.2°</td>
<td>42</td>
<td>(-1268.9)</td>
</tr>
<tr>
<td>295.6°</td>
<td>43</td>
<td>(-1345.7)</td>
</tr>
<tr>
<td>275.6°</td>
<td>44</td>
<td>(-1382.3)</td>
</tr>
<tr>
<td>253.5°</td>
<td>45</td>
<td>(-1400.0)</td>
</tr>
</tbody>
</table>

-0.00005390(t - 28)
-0.00000071035(t - 28)^2
+ 0.000000010(t - 28)^3 (17)

-0.000052899(t - 28)
-0.000000080265(t - 28)^2
+ 0.00000001813(t - 28)^3
-0.0000000001497(t - 28)^4 (18)

Table 14. Nominal emfs of saturated standard cells at some common temperatures

<table>
<thead>
<tr>
<th>Temperature (°C)</th>
<th>Acidity (H₂SO₄) of solution in cell</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>neutral*</td>
</tr>
<tr>
<td>00</td>
<td>volts</td>
</tr>
<tr>
<td>20</td>
<td>1.016936</td>
</tr>
<tr>
<td>25</td>
<td>1.018187</td>
</tr>
<tr>
<td>28</td>
<td>1.01866</td>
</tr>
<tr>
<td>30</td>
<td>1.018117</td>
</tr>
<tr>
<td>32</td>
<td>1.018041</td>
</tr>
<tr>
<td>35</td>
<td>1.017966</td>
</tr>
<tr>
<td>37</td>
<td>1.017725</td>
</tr>
</tbody>
</table>

* Actually 0.000924; 10% cadmium methodez hydrolyzes to produce H₂SO₄, of this acidity at 25°C (73).

In table 14 the nominal values of the emf of "neutral" and "acid" saturated cells are given at a series of temperatures at which cells are most frequently calibrated at the National Bureau of Standards. Exact agreement with these nominal values cannot be expected since the emfs of saturated cells are very sensitive to the acidity of the electrolyte, to the amalgam composition, and to the extent of the solubility of the glass container in the cell electrolyte; even so they have high emf stability.

Frequently, the question arises as to the effect of small changes in temperature on the emf of saturated standard cells. Table 15 lists the changes in emf that are produced by changes in temperature of only ±0.001 or ±0.01°C. The + sign for the emf refers to changes in emf produced by a decrease in temperature while the − sign for the emf refers to changes in emf produced by an increase in temperature. These data show that temperature must be controlled more accurately at the higher temperatures for comparable control of emf. They also show that for precisions of 0.5 μV the temperature must be controlled to slightly better than ±0.01°C; for 0.05 μV to better than ±0.001°C.

The emf-temperature formulas given above refer to the saturated cell as a whole, assuming that all parts of the cell are at the same temperature. The separate limbs of the cell have much larger coefficients, the negative limb having a negative coefficient and the positive limb a positive coefficient. The emf-temperature coefficient of the whole cell is the summation of those of the two limbs. The emf-temperature coefficients for each limb from 0° to 37°C are given in table 16; those given in parenthesis of the data of Sir Frank Smith [103]. The summation of those for the two limbs are given in column 4; these agree well with those calculated by International Temperature Formula. It is obvious, in view of these data, that saturated standard cells must be kept at a uniform temperature for high accuracy and precision. In table 17 are given the errors that would arise in the emf of a cell if the positive limb were at a slightly higher or slightly lower temperature than the negative limb. Also given are data for the case in which the temperature of the negative limb were slightly higher or lower temperature than the negative limb. It is for
TABLE 13. Effect of small changes in temperature on the emf of saturated standard cells at various temperatures

<table>
<thead>
<tr>
<th>Temperature °C</th>
<th>±0.001 °C</th>
<th>±0.01 °C</th>
</tr>
</thead>
<tbody>
<tr>
<td>28</td>
<td>+0.05</td>
<td>±0.5</td>
</tr>
<tr>
<td>29</td>
<td>+0.04</td>
<td>±0.4</td>
</tr>
<tr>
<td>30</td>
<td>+0.06</td>
<td>±0.6</td>
</tr>
<tr>
<td>31</td>
<td>+0.06</td>
<td>±0.6</td>
</tr>
<tr>
<td>32</td>
<td>+0.07</td>
<td>±0.7</td>
</tr>
</tbody>
</table>

+ sign for the emf refers to a decrease in temperature.
− sign for the emf refers to an increase in temperature.

TABLE 16. Temperature coefficient of positive and negative limbs of saturated standard cells and of complete cells at various temperatures

<table>
<thead>
<tr>
<th>Temperature °C</th>
<th>Negative limb</th>
<th>Positive limb</th>
<th>Complete cell</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>-0.000286</td>
<td>0.000209</td>
<td>0.000002</td>
</tr>
<tr>
<td>2</td>
<td>-0.000821</td>
<td>0.000085</td>
<td>0.000556</td>
</tr>
<tr>
<td>5</td>
<td>-0.000351</td>
<td>0.000040</td>
<td>0.000201</td>
</tr>
<tr>
<td>10</td>
<td>-0.000379</td>
<td>0.000036</td>
<td>0.000201</td>
</tr>
<tr>
<td>15</td>
<td>-0.000330</td>
<td>0.000025</td>
<td>0.000194</td>
</tr>
<tr>
<td>20</td>
<td>-0.000330</td>
<td>0.000030</td>
<td>0.000150</td>
</tr>
<tr>
<td>25</td>
<td>-0.000330</td>
<td>0.000025</td>
<td>0.000194</td>
</tr>
<tr>
<td>30</td>
<td>-0.000330</td>
<td>0.000025</td>
<td>0.000194</td>
</tr>
<tr>
<td>35</td>
<td>-0.000330</td>
<td>0.000025</td>
<td>0.000194</td>
</tr>
</tbody>
</table>

Values in parenthesis obtained by interpolation or extrapolation.

7.2. Emf Temperature Hysteresis

In general, if saturated or unsaturated standard cells are subjected to slowly changing temperatures their emf will follow closely the relations given above. If, on the other hand, the cells are subjected to abrupt temperature changes, deviations from the true emf will occur. These deviations are generally referred to as hysteresis. On cooling, the cells show first too high an emf and then a slow decrease in emf to the equilibrium value. On heating, the cells show too low an emf and then a slow rise in emf to the equilibrium values. The magnitude of the hysteresis is given by the percentage deviation from the equilibrium value and is usually greater when the temperature is decreased than when it is increased. These general relations are illustrated in figure 18 for abrupt heating of new cells from 25 to 50 °C and for abrupt cooling from 30 to 25 °C for saturated standard cells having a dE/dt of −5 μV/deg C in this temperature range. The magnitude of the hysteresis in each case is given by the distance marked by an "h" divided by the emf of the cell at the starting temper}

Figure 18. Relations showing the emf-temperature hysteresis unsaturated standards when abruptly heated or cooled 5 °C.
ans to the emf of cells under diversified conditions involving abrupt temperature changes. The magnitude of hysteresis for unsaturated cells increases with age; a cell 10 years old has about 10 times the hysteresis of a new cell. For a 5 °C abrupt change in temperature, the hysteresis of new unsaturated cells ranges from 0.02 percent (0.0001 to 0.0002 V) on cooling to 0.005 to 0.01 percent (0.00005 to 0.0001 V) on heating. The cells usually recover their emf within 1 to 2 days after cooling and 3 to 12 hours after heating. For older cells, hysteresis may persist for days or even a week.

Proportionate hysteresis is to be expected for smaller temperature intervals than 5 °C. In general, saturated cells show less hysteresis than unsaturated ones. In some cases, saturated cells do not exhibit the "overshoot" of hysteresis. Instead they approach mfs at a new temperature at an exceedingly slow rate. This phenomenon here called "lag" is not referred to as "negative hysteresis" and is attributed to the slowness in the precipitation of CdSO₄·8H₂O on cooling or to the slowness of dissolution of CdSO₄·8H₂O on heating.

Explanations have been given for hysteresis in terms of single-factor contributions. The hysteresis between the heat capacities of the two states (the cell in solubility of CdSO₄·8H₂O and the unsaturated cell) and the disturbances of temperature conditions within the cell during temperature changes must all contribute to hysteresis. Different standard cells should be maintained at 18°C temperature if at all possible. Temperature fluctuations may be kept to a minimum for unsaturated cells by placing them in temperature-lagged boxes or in Dewar flasks. A view of a temperature-lagged box used at the National Bureau of Standards in the testing of unsaturated cells is shown in figure 19.

7.3. Temperature Range

The range of temperature over which standard cells may be used is dictated by the composition of amalgam, the transition temperature of the double salt hydrates, and the freezing point of the electrolyte. The range over which amalgams of cadmium and silver amalgams of cadmium contents may be safely used is shown in figure 16. For 12.5 percent amalgam this range is 12 to 62 °C; for 10 percent amalgam it is 8 to 51 °C. Both of these amalgams may be used for a short time (2 to 3 hr) below temperatures (12.5 percent amalgam to 0 °C; 10 percent amalgam to -20 °C) or as long as the amalgams consist of two phases, solid and liquid. For work of the highest precision the cells should be confined to the temperature ranges shown.

A 15 percent amalgam should be chosen for lower temperatures, its useful range is 24 to 26 °C. For temperatures amalgams of high cadmium contents should be used, via, a 14 percent amalgam will give cells that could be used, from 24 to 67 °C. It may be possible to use unsaturated standard cells to temperatures of the boiling point of the electrolyte (slightly above 100 °C) by using amalgams of high cadmium content (above 20 percent) but these cells would not be suitable for precision work much below 80 °C.

At temperatures above 43.6 °C, even though the higher-percentage amalgams are satisfactory, saturated cells must be made with crystals of CdSO₄·H₂O since this is the stable form of solid cadmium sulfate above 43.6 °C. For unsaturated standard cells no such problem exists and attention need be given only to the composition of the amalgam.

The lower limit of use is -24 °C where the cell becomes completely frozen. Freezing begins at -17 °C. Cells completely frozen at -24 °C will behave normally after thawing if freezing has not caused a fracture in the cell. The time required for the cell to recover its normal emf may be long, however. The internal resistance of standard cells at 10 °C is about 6 times that at 25 °C, and thus increase in internal resistance may limit the use of the cell.

Significant temperatures in the use of standard cells are summarized in table 18. In practice, cells should probably be subjected to a somewhat lesser range of temperatures than shown; -16 to 40 °C is a good range for saturated cells and 4 to 40 °C for unsaturated ones.

7.4. Emf-Pressure Coefficient

The effect of pressure on the emf of a galvanic cell at constant temperature is given by

\[
\frac{dE}{dP} = \frac{-(\Delta V)_T}{nF} \text{ volt atm}^{-1}
\]  

(19)

where \(\Delta V\) is the volume change in cubic centimeters at atmospheric pressure per faraday, \(n\) is
the number of equivalents involved in the reaction, 
\( F \) is the faraday, and \( k \) is a conversion factor. 
\( 0.101325 \), which converts cubic centimeter-atmospheres into joules, i.e., volt coulombs. The volume change may be calculated from the atomic or molecular weights and the densities of the reactants and products of the reaction; for saturated standard cells this reaction is given by eq (7). At 
\( 20 \, ^{\circ}C \), the accepted densities of \( \text{Cd}, \ \text{Hg}_2\text{SO}_4, \ \text{CdSO}_4 \cdot \frac{8}{3} \text{H}_2\text{O}, \ \text{Hg} \), and a saturated solution of 
\( \text{CdSO}_4 \) are, respectively, 8.648, 7.56, and 3.090 \( \text{g cm}^{-3} \) and 13.5463 and 1.6119 \( \text{g ml}^{-1} \) [113]. Using 
these data, accepted atomic weights on the C\( ^{12} \) scale [114] and 96,487 coulombs/gram-equivalent [115]\(^{16} \) for the faraday equation 19 gives 6.4 \( \mu \text{V atm} \) for \( (d\text{E}/d\text{P}) \). This value agrees excellently with 6.1 \( \mu \text{V atm} \) found experimentally by Ramsey [116] (this value is an interpolated value, Ramsey found 5.02 \( \mu \text{V atm} \) at 20.4 \( ^{\circ}C \) and 7.6 \( \mu \text{V atm} \) at 19 \( ^{\circ}C \)).

The effect of pressure on an unsaturated cell would be nearly the same, since unsaturated cells are made with solutions that are nearly saturated.

A priori no effect on the emf of sealed cells would be expected providing the pressure was insufficient to fracture the cell. Recent experiments by Catherine Law and D. N. Craig of this Bureau, in which the external pressure on the cell was increased to approximately 5 atm, has confirmed this. Standard cells have an air space above the electrolyte which would act as a cushion to absorb pressure change even if the elasticity of the glass container were such as to transmit pressure change to the cell components.

7.5. Internal Resistance

The internal resistance in the vicinity of 25 \( ^{\circ}C \) ranges from 100 to 500 \( \Omega \) for unsaturated cells and from 500 to 1000 \( \Omega \) for saturated cells manufactured in the United States. The internal resistance increases at the rate of about 2 percent for a decrease in temperature of one degree C; this fact should be taken into account in calculating the IR drop in a cell (see table 19). The resistances of the positive and negative limbs of symmetrical H-shaped cells are approximately equal. As a cell ages its internal resistance increases slightly. The internal resistance of a standard cell may be estimated by momentarily placing a 10-M\( \Omega \) resistor across the cell terminals and reading the emf, \( E_R \). The value of the internal resistance is then given by

\[ R = 10^6(E_0 - E_R)/E_R \text{ ohms,} \quad (20) \]

where \( E_0 \) is the open-circuit emf. The cell recovers its initial emf within a few minutes after the 10-M\( \Omega \) resistor is removed. If a cell exhibits high internal resistance or insensitivity it may contain a gas bubble at the anode which may be frequently removed by tapping the cell when inclined 45\(^\circ\). If this treatment is ineffective a new cell is recommended.

7.6. Effect of Current

Standard cells are not intended to serve as sources of electric current. Even so, the question frequently arises about the effect of current on standard cells, especially the unsaturated type. When standard cells are charged or discharged the

---

\(^{16}\) In the original paper [115] values based on the physical and chemical scales of atomic weights were given. The value given here is based on an atomic weight of silver relative to the C\( ^{12} \) scale of atomic weights, namely, 107.867.

---
Table 19. Effect of current on the emf of unsaturated standard cells at 25 °C

<table>
<thead>
<tr>
<th>Current, amperes</th>
<th>Internal resistance (initial change)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>100 ohms</td>
</tr>
<tr>
<td>$10^{-10}$</td>
<td>$0.01$ μV</td>
</tr>
<tr>
<td>$10^{-9}$</td>
<td>$0.1$ μV</td>
</tr>
<tr>
<td>$10^{-8}$</td>
<td>$1$ μV</td>
</tr>
<tr>
<td>$10^{-7}$</td>
<td>$10$ μV</td>
</tr>
<tr>
<td>$10^{-6}$</td>
<td>$100$ μV</td>
</tr>
<tr>
<td>$10^{-5}$</td>
<td>$1000$ μV</td>
</tr>
</tbody>
</table>

Changes owing to changes in amalgam ($V_a$) and electrolyte ($V_e$) composition (after one year)

<table>
<thead>
<tr>
<th>$V_a$</th>
<th>$V_e$</th>
<th>$V_a$</th>
<th>$V_e$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\mu V$</td>
<td>$\mu V$</td>
<td>$\mu V$</td>
<td>$\mu V$</td>
</tr>
<tr>
<td>$10^{-10}$</td>
<td>$-$</td>
<td>$-$</td>
<td>$-$</td>
</tr>
<tr>
<td>$10^{-9}$</td>
<td>$-$</td>
<td>$-$</td>
<td>$-$</td>
</tr>
<tr>
<td>$10^{-8}$</td>
<td>$0.05$</td>
<td>$0.03$</td>
<td>$-$</td>
</tr>
</tbody>
</table>
| $10^{-7}$ | $0.1$ | $0.02$ | $2.5$ | $2.5$

Changes arising from electrode polarization (after one year)

| $10^{-10}$ | $0.1$ | $0.3$ | $3.3$ | $3.3$
| $10^{-9}$ | $0.7$ | $2.9$ | $29.3$ | $29.3$
| $10^{-8}$ | $2.3$ | $11.2$ | $112$ | $112$
| $10^{-7}$ | $26$ | $76$ | $760$ | $760$
| $10^{-6}$ | $139$ | $466$ | $4660$ | $4660$
| $10^{-5}$ | $973$ | $3184$ | $31840$ | $31840$

$^{a}$ Dash means that the change is less than 0.01 μV.

The magnitude of $V_a$ obtained on discharge at 25 °C is given by

$$V_a \text{ (in volts)} = \frac{-0.0161 I t}{FW} = -1.67 \times 10^{-6} \frac{I t}{W}$$

(23)

where $W$ is now the weight of the electrolytic solution in grams and the other symbols have the meaning given above. For unsaturated cells the weight of solution is about 100 and 20 g, respectively, for cells having internal resistances of 100 and 500 Ω. Equation (23) then becomes

$$V_a \text{ (in volts)} = -1.67 \times 10^{-8} I t$$

(24)

for the 100-Ω cell and

$$V_a \text{ (in volts)} = -6.35 \times 10^{-9} I t$$

(25)

for the 500-Ω cell.

The magnitudes of electrode polarization during discharge may be calculated, within a few microvolts, by the equation

$$\log \Delta E \text{ (in microvolts)} = 1.6048 + 0.786 \log \left( \frac{C}{A} \right)$$

(26)

where $\Delta E$ is the change in emf, in microvolts, arising from electrode polarization and changes in internal resistance, $C$ is quantity of electricity in coulombs (ampere seconds) and $A$ is apparent (geometric) electrode area in square centimeters [117]. For unsaturated cells having internal resistances of 100 and 500 Ω, $A$ is about 5.5 cm² and 1.4 cm², respectively. Some miniature types having internal resistances of about 1000 Ω and apparent surface areas of less than 1 cm² are also available. The length of time standard cells will sustain a discharge depends on the amount of material in the cells; most unsaturated cells of United States manufacture contain sufficient material to yield from 700 to 5000 coulombs if the current is kept below about $2 \times 10^{-5}$ A per cm² of electrode area.

When an external load is removed, the cells recover their initial emf, provided the discharge has not been a prolonged one. The time required for recovery depends on the severity of the discharge. For example, if an unsaturated cell (internal resistance $\approx 100$ Ω) is discharged for 5 min at $6 \times 10^{-6}$ A cm⁻² it will recover its original emf within 5 μV in 30 min and will completely recover after 6 hr. At a higher current density of $6 \times 10^{-4}$ A cm⁻² the emf will be about 180 μV below its original value after 30 min, 5 μV after 6 hr, and several days will be required for complete recovery. If the cell were discharged at a current density of $6 \times 10^{-4}$ A cm⁻² to a low cutoff voltage of 0.001 V, recovery will be exceedingly slow requiring several months and.

---

"Drop in emf is initially dictated by the $IR$ drop subsequently by a voltage change, $V_e$, with the chemical changes in the cell, electrode polarization and changes in internal resistance. For the unsaturated cell $V_a$ is made up of $V_{an}$ the change in emf associated with changes in the composition of the amalgam during charge or discharge and $V_{ae}$ the change in emf caused by the change in electrolyte content of the cell during charge or discharge. When used cells have been discharged until their internal resistance has been saturated, the latter no longer applies. The cell $V_e$ consists of $V_a$ only.

The magnitude of $V_a$ obtained on discharge at 25 °C is given by

$$V_a \text{ (in volts)} = \frac{-0.0161 I t}{FW} = -1.16 \times 10^{-8} \frac{I t}{W}$$

(21)

where $W$ is the total weight of the amalgam in grams and $F$ is the faraday (96487.0 coulombs). Unsaturated cells the total weight of amalgam is about 10 g. In this case eq (21) reduces

$$V_a \text{ (in volts)} = -1.16 \times 10^{-8} I t.$$  

(22)

unsaturated cells having internal resistances of 500 Ω the weight of the amalgam is approximately 7 and 20 g, respectively.

---

16 Includes any change in internal resistance that may occur as a cell is discharged.
Full recovery will not be attained after this prolonged period because the normal emf will have declined (see below). The time of recovery, therefore, is seen to depend on the rate and extent of the discharge.

In Table 19 changes in emf caused by various currents of low magnitude are illustrated for cells having electrode cross-sectional areas of 5.5 cm² and 1.4 cm² and internal resistances of 100 and 500 Ω. The changes arising from internal resistance are of initial changes whereas those arising from changes in amalgam composition, Vₐ, electrolyte composition, Vₑ, and electrode polarization (see footnote 16), ΔE, are functions of time of discharge (for illustration, a period of 1 year is chosen for these). The total changes in emf during a discharge is the sum of the four effects. On a current density basis it should be noted the changes for the 100-Ω and 500-Ω cells are nearly identical since the electrode area for the former cell is approximately five times that of the latter.

Standard cells may be short-circuited momentarily without permanent damage to the cells. The cells will recover their original emf within a few minutes after taken off short circuit. If kept on short circuit they will be completely discharged within 1/2 to 2 days depending on the size and internal resistance of the cell, and will not recover their initial emf. The short circuit current is given by the ratio of the open-circuit emf and the internal resistance of the cell. For cells having internal resistances of 100 Ω and 500 Ω, the short-circuit (flash) current will therefore be 1 × 10⁻² and 2 × 10⁻³ A, respectively.

7.7. Effect of Light

Mercurous sulfate is sensitive to light and changes in color at a slow rate through tan, to gray-brown, to dark brown, and finally to black. Although standard cells having discolored mercurous sulfate may have normal emfs [118] they exhibit slower approach to equilibrium values after temperature or other changes. Standard cells should, therefore, be mounted in nontransparent cases or kept in the dark and used only for short periods at a time under diffuse light.

7.8. Effect of Shock

Mechanical shocks insufficient to fracture or break or scramble the components of unsaturated standard cells have no lasting effects on the cells. Unsaturated standard cells packaged in excels and shipped by common carrier to the National Bureau of Standards have been observed to perform satisfactorily. When subjected to shocks of 10 40 g for durations of 6 to 18 msec unsaturated cells exhibit large transient changes in emf ranging from 4,200 to 31,000 µV [119]. After the shock the cell immediately recover their original emf within 2 µs. The transient emfs observed during shock probably arise from a disturbance of the mercury amalgam surfaces during the period of shock.

On the other hand, the usual types of saturated cells of United States manufacture should not be subjected to sudden shock, should not be shipped by common carrier, should be transferred by messenger, and should not be tilted more than 45°. Some new saturated standard cells of novel design are stated to be portable, i.e., may be shipped in common carrier. However, studies over a period of time will be required to ascertain the long-term stability of their emf.

7.9. Effect of Vibration

Vibrations at frequencies from 10 to 1,000 Hz (c/s) with accelerations of 1 to 10 g have no lasting effects on the emf of unsaturated standard cells [119]. During the vibration, however, rather large a-c voltages of the same frequency are generated. For an unsaturated cell having an internal resistance of 500 Ω this a-c voltage ranges from about 25 µV at 1 g and 1000 Hz to 9900 µV at 10 g and 50 Hz. Furthermore, there is a decrease in the DC emf ranging from 3 µV at 1 g and 1000 Hz to about 200 µV at 10 g and 100 Hz. In general a frequencies above 100 Hz the waveform of the a-c voltage is sinusoidal whereas below 100 Hz it is nonsinusoidal owing to the resonance of the various components of the cell. In most cases the a-c and d-c effects of the vibration appear and disappear instantaneously when vibration is started or stopped. In some instances the d-c change may be rapid in the initial moments of vibration and then build up slightly in an exponential manner for 2 or 3 minutes. In these instances when the vibration is stopped the d-c emf decays in the same fashion as it was built up.

8. Life of Standard Cells

Saturated standard cells have an exceedingly long life. Some cells at the National Bureau of Standards have been in use for nearly 60 years, and they have retained their emfs within a few microvolts; see section 2.3. On the other hand, unsaturated cells at room temperature (about 25 °C) decrease in emf at a rate of about 30 to 40 µV per year [48]. This decrease in emf is equivalent to a corrosion rate for the amalgam of about (6.8 to 13.6) × 10⁻⁷ A cm⁻². Since the emf of new unsaturated standard cells generally range from 1.01900 to 1.01940 V, depending on the concentration and acidity of the electrolyte, these cells on the average reach an emf of 1.01830 V within 23 to 37 years, providing they are maintained at 25 °C or thereabouts, and are not subjected to abuse, such as discharging or charging current; a practical life time for these cells is probably 12 to 16 years. When unsaturated standard cells reach an emf of 1.01830 V or lower the cells generally behave erratically (largely because the electrolyte may become supersaturated on cooling), have large emf-temperature coefficients, and show excessive emf-temperature hysteresis. The life of the cell is considerably reduced.
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10. Appendix 1

U.S. Law of 1894, 53d Congress, 28 Stat., Ch. 131, p. 102 (Public-105)

An Act To define and establish the units of electrical measure

enacted by the Senate and House of Representives of the United States of America in a session held that from and after the passage of this Act the legal units of electrical measure of the United States shall be as follows:

The unit of resistance shall be that which is equal to one thousand millions of the centimeter-gram-second system of the meter-ohm, and is represented by a sphere of mercury of one centimeter diameter at the temperature of ice, immersed in a column of mercury at the temperature of ice, and having a resistance of one thousand million ohms. The unit of electrical potential shall be that which is produced by a current of one milliampere flowing through a resistance of one ohm. The unit of electric current shall be that which, passing through a conductor of one square millimeter cross-sectional area and of the length of one hundred and six and three tenths centimeters, produces a force of one dyne on each meter length of the conductor.

Second. The unit of current shall be that which is known as the international ampere, which is one-tenth of the unit of current of the centimeter-gram-second system of the meter-ohm, and is practically equivalent to the ampere of the definition in the International System of Units.

Third. The unit of electro-motive force shall be that which is known as the international volt, which is the electro-motive force that, steadily applied to a
conductor whose resistance is one international ohm, will produce a current of an international ampere, and is practically equivalent to one thousand four hundred and thirty-fourths of the electro-motive force between the poles or electrodes of the voltaic cell known as Clark’s cell, at a temperature of fifteen degrees centigrade, and prepared in the manner described in the standard specifications.

Fourth. The unit of quantity shall be what is known as the international coulomb, which is the quantity of electricity transferred by a current of one international ampere in one second.

Fifth. The unit of capacity shall be what is known as the international farad, which is the capacity of a condenser charged to a potential of one international volt by one international coulomb of electricity.

Sixth. The unit of work shall be the joule, which is equal to ten million units of work in the centimeter-gram-second system, and which is practically equivalent to the energy expended in a second by an international ampere in an international ohm.

Seventh. The unit of power shall be the watt, which is equal to ten million units of power in the centimeter-gram-second system, and which is practically equivalent to the work done at the rate of one joule per second.

Eighth. The unit of induction shall be the henry, which is the induction in a circuit when the electromotive force induced in this circuit is one international volt while the inducing current varies at the rate of one Ampere per second.

Sec. 2. That it shall be the duty of the National Academy of Sciences to prescribe and publish, as soon as possible after the passage of this Act, such specifications of details as shall be necessary for the practical application of the definitions of the ampere and volt hereinbefore given, and such specifications shall be the standard specifications here mentioned.

11. Appendix 2

Public Law 617—81st Congress
(Chapter 484—2d Session)
(S. 441)
AN ACT

To redefine the units and establish the standards of electrical and photometric measurements.

Be it enacted by the Senate and House of Representatives of the United States of America in Congress assembled, That from and after the date this Act is approved, the legal units of electrical and photometric measurements in the United States of America shall be those defined and established as provided in the following sections.

SEC. 2. The unit of electrical resistance shall be the ohm, which is equal to one thousand million units of resistance of the centimeter-gram-second system of electromagnetic units.

SEC. 3. The unit of electric current shall be the ampere, which is one-tenth of the unit of current of the centimeter-gram-second system of electromagnetic units.

SEC. 4. The unit of electromotive force and of electric potential shall be the volt, which is the electromotive force that, steadily applied to a conductor whose resistance is one ohm, will produce a current of one ampere.

SEC. 5. The unit of electric quantity shall be the coulomb, which is the quantity of electricity transferred by a current of one ampere in one second.

SEC. 6. The unit of electrical capacitance shall be the farad, which is the capacitance of a capacitor that is charged to a potential of one volt by one coulomb of electricity.

SEC. 7. The unit of electrical inductance shall be the henry, which is the inductance in a circuit such that an electromotive force of one volt is induced in the circuit by variation of an inducing current at the rate of one ampere per second.

SEC. 8. The unit of power shall be the watt, which is equal to ten million units of power in the centimeter-gram-second system, and which is the power required to cause an unvarying current of one ampere to flow between points differing one volt.

SEC. 9. The units of energy shall be (a) the joule, which is equivalent to the energy supplied by a power of one watt operating for one second, and (b) the kilowatt-hour, which is equivalent to the energy supplied by a power of one thousand watts operating for one hour.

SEC. 10. The unit of intensity of light shall be the candle, which is one-sixtieth of the intensity of one square centimeter of a perfect radiator known as a “black body”, when operated at the temperature of freezing platinum.

SEC. 11. The unit of flux of light shall be the lumen, which is the flux in a unit of solid angle from a source of which the intensity is one candle.

SEC. 12. It shall be the duty of the Secretary of Commerce to establish the values of the primary electric and photometric units in absolute measure, and the legal values for these units shall be those represented by, or derived from, national reference standards maintained by the Department of Commerce.

SEC. 13. The Act of July 12, 1894 (Public Law Numbered 105, Fifty-third Congress), entitled “An Act to define and establish the units of electrical measure”, is hereby repealed.

APPROVED July 21, 1950.
12. Appendix 3

Standard Cells with Deuterium Oxide

electromotive forces of saturated standard de with deuterium oxide and normal water

<table>
<thead>
<tr>
<th>Percentage of D₂O in the water</th>
<th>Emf at 20 °C, volts</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.02%</td>
<td>1.018603</td>
</tr>
<tr>
<td>0.10</td>
<td>1.018597</td>
</tr>
<tr>
<td>0.20</td>
<td>1.018531</td>
</tr>
<tr>
<td>0.30</td>
<td>1.018495</td>
</tr>
<tr>
<td>0.40</td>
<td>1.018459</td>
</tr>
<tr>
<td>0.50</td>
<td>1.018423</td>
</tr>
<tr>
<td>0.60</td>
<td>1.018388</td>
</tr>
<tr>
<td>0.70</td>
<td>1.018344</td>
</tr>
<tr>
<td>0.80</td>
<td>1.018301</td>
</tr>
<tr>
<td>0.90</td>
<td>1.018255</td>
</tr>
<tr>
<td>100 (extrapolated from 98 percent)</td>
<td>1.018204</td>
</tr>
</tbody>
</table>

water contains 0.02 percent deuterium oxide.

(all data were reported in international volts and have been absolute volts).

elements were made with crystals of cadmium sulfate in with the respective solutions. This was accompanied by saturating each solution with anhydrous cadmium crystals that separated from the solution were then boiled with the saturated solution. The solutions were prepared to 0.04 N with respect to sulfuric acid; the above are quoted on a uniform basis of 0.04 N.

cadmium sulfate is about 8 percent less soluble in heavy water than in normal water within the temperature range of 0 to 60 °C.

13. Appendix 4

Coulometer (Brønsted) measurements* by the United States in the Physikalisch-Technische Reichsanstalt at Charlottenburg, 1931

<table>
<thead>
<tr>
<th>Experiment Number**</th>
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<tbody>
<tr>
<td>1</td>
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<tr>
<td>9</td>
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<tr>
<td>10</td>
</tr>
</tbody>
</table>

\[
E = \frac{(E + E) - \alpha D}{2} + \frac{E}{C_B} + \frac{E + E}{2} \text{ volts}
\]

(USA units) value of selected cell at 25 °C, given by

\[
M = 1.003066 \text{ volts, since (USA - PTE) ohm} = 0 \text{ ppm and (USA - PTE) volts} = -61 \text{ ppm}
\]

Studies of the changes in the difference between the emf of cells made with normal and heavy water have given supplemental evidence on the stability of the National Reference Group of Standard Cells. These studies have shown that this difference is within the spread, namely, 0.05 μV/year, discussed under item (1) in maintenance in section 2.3. However, cells made with heavy water have not, to date, shown the same internal consistency as those made with normal water, i.e., individual cells show greater day-to-day variations in emf than normal water cells.
14. Appendix 5

Constant-Temperature Oil Baths

Constant-temperature oil baths of the type used to maintain the National Reference Group of Standard Cells at a constant temperature were shown in figure 2. In this appendix a general description of a typical bath is presented. A circular bath of stainless steel or nickel-plated copper, about 75 cm in diameter and 45 cm deep, may be used all other metal parts are also of steel or nickel-plated copper to prevent the possibility of galvanic corrosion. It is filled with oil (see Appendix 6) to a depth of about 35-40 cm. The oil is stirred by a centrally located two-blade agitator which produces an upward and rotary circulation. The agitator (9) is about 48 cm in length, 5 cm wide, 0.3 cm thick, has a pitch of 20° and rotates at about 45 rpm. It is supported on a shaft (1) which is supported in ball bearing housings at the bottom and top of the bath (the one at the top is supported in a metal slab (8), about 10 cm wide and 0.3 cm thick, which rests on the central top edges of the bath. A drip cup (4) is placed on the shaft at the position shown to collect any grease that may flow down the shaft from the ball bearing housing. To guide the direction of oil circulation a metal baffle (5), 25 cm in height, is placed in the bath in the position shown in figure A1. This baffle extends to 10 cm of the bottom of the bath and slightly above the agitator. This baffle serves also to protect the cells from direct influence of the heating element and the cooling coils.

Heating is supplied by a heating coil (9) of barmanganin wire wound on a Pyrex rod having diameter of 1 cm. This rod is supported about 1 cm above the bottom of the bath by glass supports and circles the bath; its position is clearly shown in figure A1. The heating coil has a resistance of 90 ohms and operates on 110-V d-c supply.

A bank of four incandescent lamps in parallel is included in the heating circuit; two lamps operate intermittently during control while two operate continuously, i.e., some heating is provided continuously and some intermittently. Cooling coil (7), (11), as shown, are also provided. Through these coils flow oil of the same type as used in the bath. These coils are connected to similar coils in the freezing compartment of a refrigerator and the required cooling is attained by controlling the rate of oil flow. Cooling by this means is required only in emergencies or when tests of standard cells are made at temperatures below room temperature. The temperature of the bath is determined by a platinum resistance thermometer and a Mueller bridge; the thermometer is supported at the position (2) shown in the figure. The lamps in the circuit also aid an operator in determining when the bath has attained a peak temperature (one reading on Pt resistance thermometer) and

![Figure A1. Cross-sectional sketch of a constant-temperature oil bath used at the National Bureau of Standards.](image)

1 - Agitator shaft
2 - Thermometer mount
3 - Heater mount
4 - Drip cup
5 - Baffle
6 - Cell rack
7 - Cooling coils
8 - Heater
9 - Agitator
10 - Mercury-sulfide regulator
11 - Cooling coil connector
12 - Fenwall thermanovitch

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15. Appendix 6

OIL FOR CONSTANT-TEMPERATURE BATHS

The quality of the oil in which standard cells are aged is of considerable importance, and for this purpose a white mineral oil with the following properties is used:

- Odorless, tasteless;
- Viscosity: kinematic at 25 °C, 0.245;
- Density, 25 °C, 0.846;
- Refractive index, 171 °C (340 °F);
- Pour point, 207 °C (405 °F);
- Acidity (mg KOH/gm oil), none;
- Sulfur, none;
- Oxidation number, 0;
- Gum, on heating in oxygen, none;
- Discoloration, on heating in oxygen, slight orange.

Sufficiently low as to make the setting effective.

In addition this oil, when new, has a resistivity of about $3 \times 10^{14}$ ohm-cm or higher.

16. Appendix 7

CONSTANT-TEMPERATURE ENCLOSURE FOR SATURATED STANDARD CELLS

Mueller-Stimson temperature-control box described in section 5.4. In this appendix more are given. In this control box, the thermoregulator is automatically controlled by a conventional mercury-in-glass regulator. A second aluminum case, inside and thermally well insulated from it, contains saturated standard cells. The inner enclosure has a temperature very nearly the same as that of the outer case. The inner case is long, 2 1/4 inches wide, and 4 inches deep inside. The case is a casting with 1/4-in. walls and 1/4-in. bottom. A 1/4-in.-thick cover is secured to the case by numerous screws to improve thermal . The inner case is spaced within the outer case by 1/4 in. balsa wood on all six sides. The case is also a casting, with 1/8 in. sidewalls in bottom. A cover of sheet 1/8-in. aluminum is secured to the top by screws. The endwalls of the casting are plane on the side and cylindrical on the outside, the thickness at the edges being 1/8 in. and 1/4 in. at the middle; this extra thickness at the middle provides space for a vertical hole, 1/4 in. in diameter and 6 in. deep, to accommodate the thermoregulator at one end and a smaller hole to accommodate a thermometer at the other end.

The outer case is insulated with a layer of balsa wood 1 in. thick on the sides and bottom and 2 in. thick on the top. The pieces of balsa wood fit neatly into an outer wooden box. This box is of sufficient size to provide a compartment at one end to house a transformer, relay, and binding posts for the necessary connections. These accessories are mounted on a wooden panel which slides in vertical grooves in the sides of the box. The outside dimensions of the box are 8 by 13 in., by 10 in. deep, and its weight, complete, is 22 lb. A horizontal section of the control box is shown in figure A2.
The standard cells are mounted on balsa wood of appropriate size. No. 28 (0.013 in.) insulated copper wire, 4 ft. in length, is used for connections to the cell terminals. About one-third of this length is formed in a helix which is kept inside the inner case and another one-third is placed between the inner and outer cases. The wires are brought through the cases in smoothed saw cuts in the upper edges of the sides and insulated additionally with silk and glyptal whereby good thermal contact with the metal cases is assured. These turnings and lengths of wire reduce heat conduction to a negligible amount. Sheets of mica are placed on the surfaces of the aluminum case adjacent to the connecting wires, to protect them against accidental electrical grounding. Outside the outer case the wires are brought to binding posts supported on a hard-rubber strip; the positive terminal is placed on one side of the box, the negative on the other.

The thermoregulator is an adjustable mercury-glass type with a bulb 4 in. long about 13/32 in. diameter, and 8 in. long. It is covered with grea to assure good thermal contact to the reservoir into which it fits.

The heating resistor, No. 38 (0.004 in.) constant wire, has a resistance of about 70 Ω and is wound in four turns on the sides and ends of the outer aluminum case on silk fabric. One turn is placed near the top edge and another near the bottom end of the case. It operates on 20 V. A small, quiet actuating 12-V a-c relay operating on about 0.05 A is used. Power for the heater and relay is supplied by a bell-ringing transformer rated at 50 W.