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The EMF-Temperature Coefficient of "Acid" Standard Cells of the Saturated Cadmium Sulfate Type from 15 to 40° C

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This paper gives the results of new measurements of the effect of temperature on the electromotive force of standard cells of the saturated cadmium sulfate type. Measurements were made over the temperature range of 15 to 40 °C. Twelve cells of NBS manufacture and twenty-four cells supplied by two different commercial manufacturers were used in the studies. Final results were analyzed by the method of least squares using computer programs. The relation between emf and temperature for NBS, company 1, and company 2 cells was found to be given, respectively, by:

$$E_t = E_{20\,°\mathrm{C}} - [40.44\,(t-20) + 0.921\,(t-20)^2 - 0.00866\,(t-20)^3] \times 10^{-6}\ \mathrm{V},$$
$$E_t = E_{20\,°\mathrm{C}} - [40.14\,(t-20) + 0.888\,(t-20)^2 - 0.00668\,(t-20)^3] \times 10^{-6}\ \mathrm{V},$$
$$E_t = E_{20\,°\mathrm{C}} - [39.28\,(t-20) + 0.986\,(t-20)^2 - 0.00943\,(t-20)^3] \times 10^{-6}\ \mathrm{V}.$$

Values for the entropy and heat-capacity changes for the cell reaction in "acid" standard cells are also given.

Key words: EMF-temperature coefficients of standard cells; standard cells; entropy changes in standard cells; heat-capacity changes in standard cells; effect of acid on standard cells.

1. Introduction

In a recent paper [1][1] the thermodynamics of standard cells of the saturated cadmium sulfate type were given. That paper dealt with so-called "neutral" standard cells to which no sulfuric acid is intentionally added when the cell is constructed. The electromotive forces (emfs) were known in terms of the legal volt maintained by the National Bureau of Standards and the emf-temperature coefficient was that derived from the international formula [2, 3, 4] but converted to the V_{69} and t_{68} scales of voltage and temperature [1], respectively.

It is now common practice to add sulfuric acid in small amounts, between approximately 0.03 and 0.1 N (or 0.015 and 0.05 M), to standard cells to reduce the formation of the basic mercurous sulfate, $Hg_2O \cdot Hg_2SO_4$ which is formed in the hydrolysis of mercurous sulfate according to the equation:

$$2\,Hg_2SO_4(s) + H_2O(l) \rightleftharpoons Hg_2O \cdot Hg_2SO_4(s) + H_2SO_4(aq) \qquad (1)$$

where s = solid, l = liquid, and aq = aqueous. Gouy [5] and Hager and Hulett [6] found that the equilibrium concentration of H_2SO_4 formed in the hydrolysis of mercurous sulfate (eq (1)) was 0.002 N while Craig and Vinal [7] found it to be 0.00198 N at 0 °C and 0.00216 N at 28 °C thus showing that it did not change appreciably with temperature. Cadmium sulfate, the solute used to prepare the solution in a standard cell also hydrolyzes to form sulfuric acid, the equilibrium concentration being 0.00092 N at 25 °C [8]. This concentration is insufficient to prevent hydrolysis of mercurous sulfate although sometimes cadmium sulfate, especially if prepared from cadmium nitrate and sulfuric acid or digested with sulfuric acid, contains occluded sulfuric acid in sufficient amount to prevent the hydrolysis of mercurous sulfate and is therefore present through inadvertance. Usually, however, sulfuric acid in small amount is added to the cadmium sulfate electrolyte when the cells are constructed. Solutions 0.03 to 0.06 N with respect to sulfuric acid are generally used because mercurous sulfate exhibits a minimum solubility in the range from 0.04 to 0.08 N. Higher concentrations of acid cause excessive gassing at the cadmium-amalgam electrode.

Although the effect of the addition of sulfuric acid on the emf of saturated standard cells is well known [8, 9, 10, 11, 12, 13] published results do not agree as to the effect of the addition of sulfuric acid on the emf-temperature coefficient. Obata and Ishibashi [14] determined the emf-temperature coefficient of acid cells over a wide range of acidities, namely, 0.078 to 0.756 N and for temperatures from 15.67 to 29.57 °C and concluded that "the use of the acid electrolyte

[1] Figures in brackets indicate the literature references at the end of this paper.

has very little effect on the temperature coefficient of the cell; the cell containing an electrolyte acidified to 0.76 *N* [too high for emf stability] has a temperature coefficient only 11 percent larger than the neutral one." For 0.078 *N* their value of $-42.5\ \mu V$ for dE/dT at 20 °C may be compared with $-40.64\ \mu V$ for the neutral cell [1]; it is evident, therefore, that their results even for low acidity show that addition of acid increases the emf-temperature coefficient.

However, Vosburgh and Eppley [15] stated that a cell made with saturated cadmium sulfate to which 0.015 *M* sulfuric acid was added had the same emf-temperature coefficient as the neutral cell, while they later [16] stated that the change in emf between 25 and 35 °C for *some* cells with electrolytes containing 0.01 mol sulfuric acid per liter of solution is slightly less than that of neutral cells. Also later, Vosburgh [17] after measuring the emf of acid cells from 15 to 40 °C stated that "Wolff's temperature formula was found to hold for all [cells], the presence of acid being found to have little or no effect on the temperature coefficient." Vosburgh had used cells with sulfuric acid concentrations of 0.021, 0.035, 0.048, 0.064, and 0.078 mol per liter. Also the National Physical Laboratory [18] stated that the temperature coefficients of standard cells of acidities from 0.05 to 0.5 *N* show no particular correlation with the acidity.

At about the same time this latter work was done, the Electrotechnical Laboratory of Japan [12] also investigated the effect of acid on the emf-temperature coefficient of saturated standard cells; acidities ranged from 0.008 to 1.0 *N* and the temperature range was 15 to 30 °C. Ishibashi and Ishizaki [12] who conducted the investigation found that the emf-temperature coefficients of cells with electrolytes of low acidity were irregular and some of them were smaller than those for neutral cells. They also stated that "the cells acidified up to 0.08 mol/liter (0.16 *N*) have practically the same temperature coefficient of emf as given by Wolff and Waters' equation, so far as the accuracy of only 0.005 percent is required [i.e., the same as neutral cells]. The coefficient for separate cells, however, must be determined whenever the accuracy of about 0.001 percent is required."

Vigoureux and Watts [19] also measured the emf of "acid" cells as a function of temperature over the range of -20 to 40 °C. The solvent for the electrolyte, $CdSO_4 \cdot \frac{8}{3} H_2O$, in these cells was decinormal sulfuric acid; therefore, the cell acidity was 0.077 *N*. Vigoureux and Watts did not, however, give comparisons with "neutral" cells except to cite reference [18] to the effect that the acidity of the electrolyte does not affect the temperature coefficient to an appreciable extent.

2. Experimental Detail

Owing to the various results reported above on the emf-temperature coefficients of "acid" standard cells of the saturated cadmium sulfate type and the increased use of "acid" cells it was decided to make new measurements of the emf-temperature coefficient of the "acid" type of cell. Accordingly, 12 cells made at NBS in December 1955 were selected for the study. These cells were made with 10 percent cadmium amalgam, electrolytic mercurous sulfate, and crystals of $CdSO_4 \cdot \frac{8}{3} H_2O$ having a diameter of about 2 to 4 mm. The saturated solution of cadmium sulfate was acidified to 0.021 *N* by the addition of sulfuric acid. The cells were of the H-form and were assembled as outlined in reference [8]; see also references [20] and [21] for descriptions of the preparations of saturated standard cells at the National Bureau of Standards. These cells were also used in 1966 in the transfer of the "volt standard" from the old NBS site in Washington to the new NBS site in Gaithersburg, Md. [22, 23].

In addition two different manufacturers of standard cells each supplied 12 "acid" saturated standard cells for the study. These are subsequently referred to as commercial 1 cells or C1 cells and as commercial 2 cells or C2 cells. These cells were about 2 years old at the start of the study. They were also of the H-form and were made with 10 percent cadmium amalgam and electrolytic mercurous sulfate. The C1 cells had a stated acidity of 0.061 *N* (except cell C1B which was replaced by one of acidity of 0.044 *N* for the measurements in Gaithersburg, Md.; the former one of acidity of 0.061 *N* was broken in transit from Washington, D.C. to Gaithersburg, Md.) and were made with crystals of $CdSO_4 \cdot \frac{8}{3} H_2O$ of 4, 8, and 10 mm in diameter. The C2 cells had a stated acidity of 0.025 *N* and the crystals of $CdSO_4 \cdot \frac{8}{3} H_2O$ over the mercurous sulfate paste had a consistency of granulated sugar while those over the amalgam consisted of a mixture of crystals of the consistency of granulated sugar and of larger crystals about 8 mm in diameter. The depth of mercurous paste was about 1.3 cm in NBS cells, 1.5 cm in C1 cells, and 1.7 cm in C2 cells.

Studies of the effect of temperature on the emf of these 36 cells were started in December 1961. The cells were housed in an oil bath maintained within ± 0.001 °C at each of the temperatures used in the study on the day measurements of the emf were made. The temperatures were read with a calibrated Pt-resistance thermometer and the emfs were measured to 0.1 μV with a Brooks comparator [24]. After a change in temperature the cells were maintained at least one week at the new temperature before readings of the emf were taken. At least ten readings over a period of two weeks were made at each temperature. The sequence of the temperatures, the groups of cells used at each temperature, and the time interval from the termination of the last of the initial readings at 28 °C to the time of the last readings at subsequent temperatures are given in table 1.

Various interruptions, most notably the move of NBS from Washington, D.C. to Gaithersburg, Md., in 1966, delayed completion of the study until September,

TABLE 1. *Sequence of measurements*

Sequence of temperatures	Groups of cells	Time intervals (days)* for		
		NBS cells	C1 cells	C2 cells
Washington, D.C.				
28 °C	NBS, C1, C2	0	0	0
32 °C	NBS, C1, C2	42	59	44
35 °C	NBS, C1, C2	108	105	108
38 °C	NBS, C1, C2	147	147	147
40 °C	NBS, C1, C2	190	197	190
35 °C	NBS, C1, C2	253	266	265
28 °C	NBS, C1, C2	351	352	351
20 °C	NBS, C1, C2	506	507	506
20 °C	NBS, C1, C2	625	629	628
25 °C	NBS, C1, C2	741	742	741
Gaithersburg, Md.				
15 °C	C1, C2	....	1938	1937
25 °C	NBS	2246	....	....
20 °C	NBS	2303	....	....
15 °C	NBS	2414	....	....

*From final date at one temperature to final date at subsequent temperature.

1968. Owing to the time period, about 7 years, consumed in the study, the cells showed slight drifts in emf with time. These were made evident by comparing the mean emf of the 12 cells of each group at those temperatures where second sets of measurements were made. The average changes or drift rates were found to be 3.62×10^{-9} V/day for the NBS cells,[2] 2.71×10^{-9} V/day for the C1 cells, and 9.6×10^{-10} V/day for the C2 cells.

First the observed emfs without drift-rate corrections were fitted to the third-order equation:[3]

$$E_t = E_{20\,^\circ\mathrm{C}} + \alpha(t-20) + \beta(t-20)^2 + \gamma(t-20)^3 \tag{2}$$

by the method of least squares using a computer program: $E_{20\,^\circ\mathrm{C}}$ is the emf at 20 °C and α, β, and γ are constants. The values of α, β, and γ for the NBS, C1, and C2 cells are given, respectively, in tables 2, 3, and 4. The mean standard deviations are given for α, β, and γ and the uncertainties in the fit, 1σ, are standard deviations of the fit of the data to equation (2). Corrections for drifts in emf with time were then made for each cell. These were obtained from the equation:

$$E'-E=\Delta E=\alpha'(t-20)+\beta'(t-20)^2+\gamma'(t-20)^3 \tag{3}$$

where E' is the corrected emf and $\alpha'=\alpha+\Delta$, $\beta'=\beta+\Delta$, and $\gamma'=\gamma+\Delta$ with Δ being the correction to the constants of eq (2). The final values for the constants for each cell and the averages are given within the parentheses in tables 2, 3, and 4.

Final recommended values for α, β, and γ for each type of cell are given at the bottom of tables 2, 3, and 4; data for cell C2J were omitted in arriving at a final value owing to the large standard deviation of the fit to eq (2). Thus, for NBS cells of 0.021 N acidity,

$$E_t = E_{20\,^\circ\mathrm{C}} - [40.44(t-20) + 0.921(t-20)^2 - 0.00866(t-20)^3] \times 10^{-6}\mathrm{V} \tag{4}$$

TABLE 2. *Coefficients in the equation:* $E=E_{20°C}+\alpha(t-20)+\beta(t-20)^2+\gamma(t-20)^3$ *for National Bureau of Standards cells*

Cell No.	$E_{20\,^\circ\mathrm{C}}$ V	(On V_{69} and t_{68} scales)			
		α μV	β μV	γ μV	σ μV
NBS1157	#a 1.0186569(4)	*− 40.4096(.01)	*− 0.9271(.008)	*0.0077(.00070)	1.3194
NBS1158	1.0186598(3)	− 40.4076(.01)	− 0.9498(.003)	.0086(.00061)	1.2891
NBS1159	1.0186597(3)	− 40.4971(.01)	− 0.9304(.007)	.0080(.00069)	1.3941
NBS1160	1.0186599(4)	− 40.4061(.01)	− 0.9260(.005)	.0077(.00063)	1.0890
NBS1161	1.0186619(6)	− 40.7635(.02)	− 0.9221(.010)	.0080(.00136)	1.9925
NBS1162	1.0186507(3)	− 40.2162(.01)	− 0.9216(.003)	.0075(.00060)	1.0133
NBS1163	1.0186528(2)	− 40.3923(.01)	− 0.9194(.002)	.0077(.00054)	1.4056
NBS1164	1.0186580(6)	− 40.6369(.01)	− 0.9221(.008)	.0081(.00099)	1.7193
NBS1165	1.0186529(4)	− 40.6680(.01)	− 0.8893(.008)	.0069(.00070)	1.5041
NBS1166	1.0186549(1)	− 40.7567(0)	− 0.8840(0)	.0067(.00032)	1.3328
NBS1167	1.0186602(6)	− 40.1705(.01)	− 1.0128(.009)	.0114(.00104)	2.3725
NBS1168	1.0186537(2)	− 40.1258(0)	− 0.9170(.001)	.0071(.00035)	0.5679
mean	1.0186564(4)	− 40.4542(.01)	− 0.9268(.005)	.0080(.00071)	....
σ_m	....	0.0630	0.0093	.00035	1.4847
final	....	− 40.44	− 0.921	0.00866	1.5

Values within parentheses are negative.
* All values within parentheses are positive corrections for drift in emf with time.
[a] Values in parentheses for this column are corrections for the last decimals in the emf or should be multiplied by 10^{-7}.

[2] Earlier observations, from December 1955 to December 1961 also gave this drift rate for these cells.

[3] Inspections showed that a second-order equation was inadequate whereas a fourth-order equation gave no better fit to the experimental data than a third-order equation.

TABLE 3. *Coefficients in the equation:* $E = E_{20\,^{\circ}C} + \alpha\,(t-20) + \beta\,(t-20)^2 + \gamma\,(t-20)^3$ *for Company 1 cells*

Cell No.	$E_{20\,^{\circ}C}$ V	(On V_{69} and t_{68} scales) α μV	β μV	γ μV	σ μV
C1A	# [a] 1.0186005(8)	*−40.1148(0)	*−0.8902(.001)	*0.0061(.00008)	0.4947
C1B	1.0185969(24)	−40.5868(0)	−0.8039(.001)	.0031(.00033)	.4359
C1C	1.0185995(27)	−40.1137(.01)	−0.8963(.001)	.0064(.00035)	.6385
C1D	1.0186021(43)	−40.2768(.01)	−0.8933(.003)	.0065(.00050)	.8085
C1E	1.0185992(45)	−40.4774(.01)	−0.8608(.003)	.0055(.00054)	.6251
C1F	1.0186026(51)	−40.3271(.01)	−0.9174(.004)	.0073(.00058)	.7664
C1G	1.0186006(32)	−40.0042(.01)	−0.9063(.001)	.0067(.00042)	.2867
C1H	1.0186011(61)	−40.1528(.01)	−0.8850(.007)	.0060(.00059)	.3872
C1I	1.0186007(40)	−39.9425(.01)	−0.9064(.002)	.0067(.00050)	.4037
C1J	1.0186000(32)	−39.8191(.01)	−0.9244(.001)	.0072(.00042)	.7741
C1K	1.0185987(37)	−39.9253(.01)	−0.9095(.002)	.0067(.00046)	.7795
C1L	1.0185999(67)	−40.0702(.01)	−0.9015(.008)	.0067(.00062)	.5839
mean	1.0186002(38)	−40.1509(.01)	−0.8913(.003)	.0062(.00044)	....
σ_m	....	0.0662	0.0093	0.00029	0.6067
final	....	−40.14	−0.888	0.00668	0.6

\# Values within parentheses are negative
*All values within parentheses are positive corrections for drift in emf with time.
[a] Values in parentheses for this column are corrections for the last decimals in the emf or should be multiplied by 10^{-7}.

TABLE 4. *Coefficients in the equation:* $E = E_{20\,^{\circ}C} + \alpha\,(t-20) + \beta\,(t-20)^2 + \gamma\,(t-20)^3$ *for Company 2 cells*

Cell No.	$E_{20\,^{\circ}C}$ V	(On V_{69} and t_{68} scales) α μV	β μV	γ μV	σ μV
C2A	[a] 1.0186219(52)	*−38.8723(.01)	−1.0420(.005)	0.0109(.00060)	1.9416
C2B	#1.0186231(21)	−39.6109(0)	−0.9413(.001)	.0075(.00031)	1.1653
C2C	1.0186221(4)	−39.4001(0)	−0.9683(0)	.0084(.00007)	1.5217
C2D	#1.0186220(10)	−40.2280(0)	−0.8616(0)	#.0051(.00018)	0.8837
C2E	1.0186223(31)	−38.9803(.01)	−1.0480(.001)	.0112(.00045)	1.7775
C2F	1.0186214(31)	−39.3767(.01)	−0.9904(.001)	.0095(.00045)	1.3334
C2G	1.0186254(15)	−39.2822(0)	−0.9942(.001)	.0094(.00020)	1.6330
C2H	1.0186199(23)	−38.9568(.01)	−1.0350(.001)	.0106(.00031)	1.8220
C2I	#1.0186169(42)	−40.2187(.01)	−0.8390(.003)	.0040(.00053)	2.0724
C2J	#1.0186041(368)	#−39.9149(1.45)	#−0.7728(.240)	.0008(.00950)	7.2131
C2K	1.0186217(46)	−38.5832(.01)	−1.0853(.004)	.0124(.00054)	2.5660
C2L	#1.0186218(4)	−38.7256(0)	−1.0649(0)	#.0115(.00007)	2.3618
mean	#1.0186202(20)	#−39.3458(.12)	#−0.9702(.019)	.0084(.00035)	....
σ_m	....	0.1669	0.0262	.00101	2.7024
mean-C2J	1.0186217(11)	−39.2941(.01)	−0.9882(.002)	.0091(.00029)	....
σ_m	....	0.1669	0.0243	.00081	1.7991
final	....	−39.28	−0.986	.00943	1.8

\# Values within parentheses are negative.
*All values within parentheses are positive corrections for drift in emf with time unless noted.
[a] Values in parentheses for this column are corrections for the last decimals in the emf or should be multiplied by 10^{-7}.

for C1 cells of 0.061 N acidity,

$$E_t = E_{20\,^{\circ}C} - [40.14(t-20) + 0.888(t-20)^2 - 0.00668(t-20)^3] \times 10^{-6}\text{V} \quad (5)$$

for C2 cells of 0.025 N acidity,

$$E_t = E_{20\,^{\circ}C} - [39.28(t-20) + 0.986(t-20)^2 - 0.00943(t-20)^3] \times 10^{-6}\text{V}. \quad (6)$$

At about the same time covered by this investigation, Froehlich and Melchert, with the assistance of Steiner, in the laboratories of the Physikalisch-Technische Bundesanstalt, also carried out a study of the emf-temperature coefficient of "acid" standard cells over the range of 10 to 30 °C and published their results in April, 1971 [25]. The pH of the electrolyte used in the cells was 1.4±0.2; the hydrogen-ion activity was, therefore, of the order of 0.04. No concentration value was given; from known values of the activity coefficient of saturated cadmium sulfate solution, namely, 0.03641 [1] and of sulfuric acid of the same ionic strength, namely, 0.208 [26], and the density of the saturated solution [27] the normality calculated from the pH value given by Froehlich and Melchert would appear to be about 0.26 N. However, the emfs given for 20 °C by Froehlich and Melchert indicate that the acidity was about 0.03–0.04 N. Ten cells were used in the study, two each of about three, four, five, seven, and nine years old at the time of the measurements. The emfs at 20 °C ranged from 1.0186053 V to 1.0186457 V; no correlation with pH was given, however, a relation between E and dE/dT may be calculated from their data and is shown later.

From the results obtained for the ten cells over a temperature range of 10 to 30 °C and taking cognizance of drifts in emf with time, Froehlich and Melchert [25] arrived at:

$$E_t = E_{20\,^\circ\mathrm{C}} - [39.78(t-20) + 0.936(t-20)^2 - 0.0086(t-20)^3] \times 10^{-6}\mathrm{V} \qquad (7)$$

for the relation between emf and temperature.

In table 5, values for dE/dT from 15 to 40 °C are given for NBS, C1, and C2 cells. The standard deviation, σ, of an individual value and the standard deviation of the mean, σ_m, are also given. The values of dE/dT given by the international formula (Int), the equation of Vigoureux and Watts (VW), and of Froehlich and Melchert (FM) are given for comparison. Also the mean emfs are given at the bottom of the table.

Inspection of the data shows that there is no correlation between dE/dT and the normality of the solution. This is clearly shown in figure 1 for values of dE/dT at 20 °C; similar results are found for the other temperatures. It is evident, as was stated earlier by Ishibashi and Ishizaki [12] that the emf-temperature coefficients of cells with electrolytes of low acidity are irregular. Since the emf is decreased by the addition of acid it remains that dE/dT may be a function of the emf. This is shown not to be the case in figure 2 where dE/dT at 20 °C is plotted against the emf at 20 °C; 10.5 μV (see ref. [8] for this factor) were subtracted from the emfs of Ishibashi and Ishizaki to place their emfs on the United States of America base of reference for the volt. It is evident from figure 2 that there is no clear correlation between E and dE/dT over the acidity range of 0 to 0.06 N. As also stated earlier by Ishibashi and Ishizaki for a precision of 0.005 percent the addition of acid has little or no effect on dE/dT while for a precision of 0.001 percent the individual values of dE/dT must be experimentally determined. Furthermore, drift rates must be determined if the highest precision is required.

One point is significant in figure 2, namely, that some of the emf data of NBS and ETL at 20 °C exceed that normally attributed to "neutral" cells and that some of the emfs reported by Froehlich and Melchert are very close to that for the so-called "neutral" cell. The international value of the emf of "neutral" cells was based on the measurements made with cells with chemically prepared and with dc-electrolytic mercurous sulfate. Wolff and Waters [2] showed that dc-electrolytic mercurous sulfate, on the average, gave cells with emfs exceeding by 16.8 μV those made with chemically prepared mercurous sulfate. Since dc-electrolytic mercurous sulfate was used in the cells discussed herein, this value of 16.8 μV was added to the international value and is designated as "corrected emf" in figure 2. With this correction the emfs of the NBS cells approximate that of the so-called "neutral" cell; apparently, the acid in the cells is largely neutralized by the alkaline constituent of the glass container during the aging period (this is exhibited by the upward drift in emf with time, as mentioned earlier in this paper).

Finally in table 6 values of the second derivative, d^2E/dT^2, and in table 7 values of the entropy and heat-capacity changes for the cell reaction in "acid"

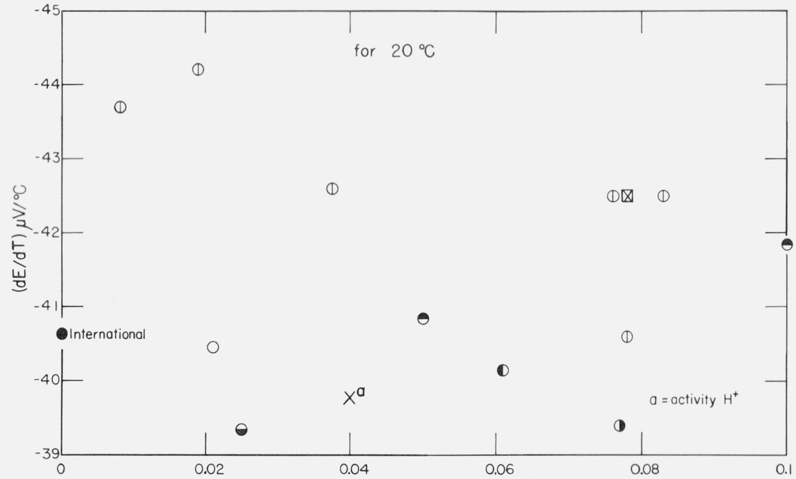

FIGURE 1. *Emf-temperature coefficients of saturated standard cells and the normality of sulfuric acid in the electrolyte in the cell.*

○—National Bureau of Standards [1].
◒—National Physical Laboratory [18].
⦶—Electrotechnical Laboratory, Tokyo [12].
×—Physikalisch-Technische Bundesanstalt [25].
◑—Vigoureux and Watts [19].
⊠—Obata and Ishibashi [14].
◐—Company 1.
◓—Company 2.
●—International formula [2,3,4].

TABLE 5. *Emf-temperature coefficients of "acid" standard*

No.*	15 °C			20 °C			25 °C		
	NBS	C1	C2	NBS	C1	C2	NBS	C1	C2
1	− 30.60	− 30.76	− 27.63	− 40.42	− 40.11	− 38.86	− 48.98	− 48.54	− 48.37
2	− 30.24	− 32.30	− 29.62	− 40.40	− 40.59	− 39.61	− 49.17	− 48.36	− 48.43
3	− 30.60	− 30.64	− 29.08	− 40.49	− 40.10	− 39.40	− 49.07	− 48.55	− 48.45
4	− 30.56	− 30.84	− 31.24	− 40.40	− 40.27	− 40.23	− 48.98	− 48.64	− 48.48
5	− 30.92	− 31.44	− 27.63	− 40.74	− 40.47	− 38.97	− 49.16	− 48.59	− 48.57
6	− 30.41	− 30.59	− 28.73	− 40.21	− 40.32	− 39.37	− 48.78	− 48.86	− 48.51
7	− 30.59	− 30.41	− 28.63	− 40.38	− 39.99	− 39.28	− 48.94	− 48.51	− 48.49
8	− 30.80	− 30.87	− 27.79	− 40.63	− 40.14	− 38.95	− 49.09	− 48.43	− 48.47
9	− 31.28	− 30.35	− 31.51	− 40.66	− 39.93	− 40.21	− 48.90	− 48.44	− 48.23
10	− 31.39	− 30.00	[c](− 30.46)	− 40.76	− 39.81	[c](− 41.36)	− 49.07	− 48.47	[c](− 50.72)
11	− 29.19	− 30.30	− 26.79	− 40.16	− 39.92	− 38.57	− 49.27	− 48.45	− 48.42
12	− 30.41	− 30.58	− 27.22	− 40.13	− 40.06	− 38.73	− 48.73	− 48.45	− 48.52
mean	− 30.58	− 30.76	[c]− 28.72	− 40.45	− 40.14	[c]− 39.29	− 49.01	− 48.52	[c]− 48.45
σ	0.557	0.410	1.559	0.216	0.232	0.554	0.159	0.092	0.090
σ_m	.161	.118	.470	.062	.067	.167	.046	.027	.027
Int.		[a]− 30.39(.04)			− 40.64(.04)			− 40.39(.04)	
VW		[b]− 29.79(.71)			− 39.40(.55)			− 48.02(.55)	
FM		[a]− 29.78(.06)			− 39.78(.05)			− 48.50(.03)	
E(NBS)		1.0188353			1.0186572			1.0184331	
E(C1)		1.0187817			1.0186040			1.0183819	
E(C2)		[c] 1.0187934			[c] 1.0186228			[c] 1.0184029	
FM		1.0187982			1.0186238			1.0184026	
Int.		1.0188224			1.0186442			1.0184185	

* Numbers are in sequence for cells NBS, C1, and C2 given in tables 2, 3, and 4.
[a] Values in parentheses are σ_m, standard deviation of the mean.
[b] Maximum uncertainty of deviations from given formula.
[c] Eleven cells only; data for cell No. 10 omitted.
[d] Vigoureux and Watts gave only the differences between emfs at a particular temperature and emfs of reference cells at 20 °C.

TABLE 6. *The second derivative*, d^2E/dT^2

No.*	15 °C			20 °C			25 °C		
	NBS	C1	C2	NBS	C1	C2	NBS	C1	C2
1	− 2.090	− 1.964	− 2.419	− 1.838	− 1.778	− 2.074	− 1.586	− 1.593	− 1.729
2	− 2.170	− 1.711	− 2.115	− 1.894	− 1.606	− 1.881	− 1.617	− 1.501	− 1.646
3	− 2.108	− 1.993	− 2.191	− 1.847	− 1.791	− 1.937	− 1.586	− 1.588	− 1.683
4	− 2.092	− 1.991	− 1.871	− 1.842	− 1.781	− 1.723	− 1.592	− 1.571	− 1.676
5	− 2.105	− 1.897	− 2.444	− 1.824	− 1.716	− 2.094	− 1.543	− 1.534	− 1.745
6	− 2.080	− 2.063	− 2.277	− 1.837	− 1.827	− 1.979	− 1.594	− 1.590	− 1.680
7	− 2.082	− 2.024	− 2.274	− 1.835	− 1.811	− 1.986	− 1.588	− 1.597	− 1.698
8	− 2.101	− 1.954	− 2.395	− 1.828	− 1.756	− 2.068	− 1.556	− 1.558	− 1.741
9	− 1.991	− 2.025	− 1.808	− 1.763	− 1.809	− 1.672	− 1.535	− 1.593	− 1.536
10	− 1.979	− 2.075	(− 2.335)	− 1.768	− 1.847	(− 2.026)	− 1.557	− 1.618	(− 1.717)
11	− 2.381	− 2.030	− 2.551	− 2.008	− 1.815	− 2.163	− 1.634	− 1.600	− 1.774
12	− 2.056	− 2.004	− 2.473	− 1.832	− 1.787	− 2.130	− 1.509	− 1.570	− 1.787
mean	− 2.103	− 1.978	[c]− 2.256	− 1.843	− 1.777	[c]− 1.973	− 1.575	− 1.576	[c]− 1.709
σ	0.088	0.096	0.212	0.058	0.064	0.159	0.036	0.031	0.070
σ_m	.025	.028	.067	.017	.019	.048	.010	.009	.021
Int.		[a]− 2.200(.005)			− 1.900(.003)			− 1.600(.003)	
VW		[b]− 2.049(.08)			− 1.806(.06)			− 1.653(.06)	
FM		− 2.130(.007)			− 1.872(.004)			− 1.614(.007)	

*Numbers are in sequence for cells NBS, C1, and C2 given in tables 2, 3, and 4.
[a] Values in parentheses are σ_m, standard deviation of the mean.
[b] Maximum uncertainty of deviations from given formula.
[c] Eleven cells only; data for cell No. 10 omitted.

cells of the saturated cadmium sulfate type, μV/°C

30 °C			35 °C			40 °C		
NBS	C1	C2	NBS	C1	C2	NBS	C1	C2
− 56.28	− 56.04	− 56.15	− 62.32	− 62.62	− 62.21	− 67.10	− 68.27	− 66.54
− 56.57	− 55.62	− 56.07	− 62.58	− 62.36	− 62.55	− 67.22	− 68.59	− 67.85
− 56.35	− 55.98	− 56.23	− 62.32	− 62.41	− 62.73	− 67.00	− 67.82	− 67.97
− 56.32	− 55.97	− 55.98	− 62.40	− 62.25	− 62.76	− 67.24	− 67.48	− 68.79
− 56.18	− 55.81	− 56.42	− 61.79	− 62.12	− 62.52	− 66.00	− 67.53	− 66.87
− 56.15	− 56.22	− 56.17	− 62.30	− 62.40	− 62.33	− 67.23	− 67.40	− 67.00
− 56.08	− 55.96	− 56.27	− 62.34	− 62.35	− 62.60	− 67.19	− 67.66	− 67.49
− 56.18	− 55.73	− 56.35	− 61.91	− 62.03	− 62.60	− 66.28	− 67.35	− 67.21
− 56.00	− 55.86	− 55.57	− 61.97	− 62.20	− 62.23	− 66.79	− 67.47	− 68.21
− 56.33	− 55.99	[c](− 58.53)	− 62.54	− 62.37	[c](− 64.80)	− 67.69	− 67.60	[c](− 69.52)
− 56.50	− 55.92	− 56.32	− 61.88	− 62.31	− 62.28	− 66.75	− 67.62	− 66.30
− 56.21	− 55.76	− 56.59	− 62.58	− 61.98	− 62.96	− 67.83	− 67.12	− 67.61
− 56.26	− 55.91	[c]− 56.19	− 62.24	− 62.28	[c]− 62.52	− 67.03	− 67.66	[c]− 67.44
0.165	0.160	0.262	0.284	0.179	0.241	0.521	0.405	0.688
.048	.046	.079	.082	.052	.073	.150	.117	.297
	− 56.63(.04)			− 62.37(.06)			− 66.60(.09)	
	[e]− 56.10(.63)			[e]− 64.08(.70)			[e]− 72.41(.70)	
	− 55.92							
Electromotive forces [d]								
	1.0181694			1.0178726			1.0175493	
	1.0181205			1.0178246			1.0174994	
	[c] 1.0181408			[c] 1.0178436			[c] 1.0175182	
	1.0181410							
	1.0181528			1.0178547			1.0175317	

[e] Based on four cells only; Vigoureux and Watts considered their results above 28 °C to be less reliable than those for lower temperatures.
Int. International formula [2, 3, 4].
VW Vigoureux and Watts [19].
FM Froehlich and Melchert [25].

for saturated standard cells, μV/°C/°C

30 °C			35 °C			40 °C		
NBS	C1	C2	NBS	C1	C2	NBS	C1	C2
− 1.334	− 1.408	− 1.384	− 1.082	− 1.222	− 1.039	− 0.830	− 1.037	− 0.694
− 1.341	− 1.396	− 1.412	− 1.065	− 1.291	− 1.078	− 0.788	− 1.186	− 0.943
− 1.325	− 1.386	− 1.428	− 1.065	− 1.183	− 1.174	− 0.804	− 0.981	− 0.920
− 1.342	− 1.361	− 1.428	− 1.092	− 1.151	− 1.280	− 0.842	− 0.941	− 1.133
− 1.263	− 1.353	− 1.395	− 0.982	− 1.172	− 1.046	− 0.701	− 0.991	− 0.696
− 1.351	− 1.354	− 1.381	− 1.108	− 1.118	− 1.083	− 0.865	− 0.881	− 0.784
− 1.340	− 1.383	− 1.410	− 1.093	− 1.170	− 1.122	− 0.846	− 0.956	− 0.834
− 1.283	− 1.361	− 1.413	− 1.010	− 1.163	− 1.086	− 0.737	− 0.965	− 0.759
− 1.307	− 1.377	− 1.400	− 1.079	− 1.161	− 1.264	− 0.851	− 0.945	− 1.128
− 1.347	− 1.390	(− 1.408)	− 1.136	− 1.161	(− 1.099)	− 0.926	− 0.932	(− 0.790)
− 1.261	− 1.385	− 1.386	− 0.888	− 1.171	− 0.998	− 0.515	− 0.956	− 0.610
− 1.385	− 1.353	− 1.444	− 1.162	− 1.136	− 1.101	− 0.938	− 0.919	− 0.758
− 1.323	− 1.392	− 1.408	− 1.072	− 1.177	− 1.116	− 0.804	− 0.974	− 0.842
0.038	0.080	0.020	0.068	0.044	0.105	0.113	0.077	0.172
.011	.023	.006	.020	.013	.032	.033	.022	.052
	− 1.300(.003)			− 1.000(.005)			− 0.700(.008)	
	− 1.590(.07)			[d]− 1.617(.08)			[d]− 1.734(.09)	
	− 1.356(.013)			....			....	

[d] Vigoureux and Watts gave only differences between emfs at a particular temperature and emf of reference cells at 20 °C.
Int. International formula [2, 3, 4].
VW Vigoureux and Watts [19].
FM Froehlich and Melchert [25].

TABLE 7. *Entropy and heat-capacity changes for the reaction in "acid" standard cells of the saturated cadimum sulfate type*

	Acidity N	15 °C	20 °C	25 °C	30 °C	35 °C	40 °C
		Entropy changes, J K^{-1} mol^{-1}					
International [2,3,4]	0.00092	−5.86	−7.84	−9.53	−10.93	−12.04	−12.85
NBS	.021	−5.90	−7.81	−9.46	−10.86	−12.01	−12.94
FM	*	−5.75	−7.68	−9.36	−10.79	...	...
C2	.025	−5.54	−7.58	−9.35	−10.84	−12.06	−13.01
C1	.061	−5.94	−7.75	−9.36	−10.79	−12.02	−13.06
VW	.077	−5.75	−7.60	−9.27	[a](−10.83)	[a](−12.37)	[a](−13.97)
Thermochemical [1]	0	...	...	−9.58	...	...	...
		Heat-capacity changes, J K^{-1} mol^{-1}					
International [2,3,4]	0.00092	−122.33	−107.48	−92.06	−76.05	−59.46	−42.30
NBS	.021	−116.94	−104.26	−90.62	−77.40	−63.75	−48.59
FM	*	−118.44	−105.90	−92.86	−79.33	...	...
C2	.025	−125.45	−111.71	−98.33	−82.37	−66.36	−50.88
C1	.061	−109.99	−101.64	−90.68	−81.43	−69.99	−58.96
VW	.077	−113.94	−102.17	−95.10	[a](−93.02)	[a](−96.15)	[a](−104.79)
Thermochemical [1]	0	...	...	−93.72	...	...	...

* pH = 1.4 ± 0.2; $a_{H^+} \approx 0.04$.
[a] Based on four cells only [19].

International — International formula [2,3,4].
FM Froehlich and Melchert [25].
VW Vigoureux and Watts [19].

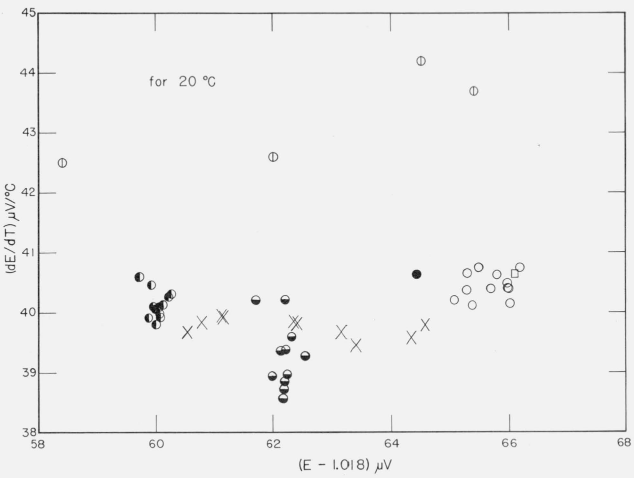

FIGURE 2. *Emf-temperature coefficients of saturated standard cells and the emf of the cell.*

○—National Bureau of Standards [1].
⦶—Electrotechnical Laboratory, Tokyo [12].
×—Physikalisch-Technische Bundesanstalt [25].
◐—Company 1.
◒—Company 2.
●—International formula [2,3,4].
□—Corrected international emf.

standard cells are given. The entropy change for the "acid" cells is in all cases less than those observed for the so-called "neutral" cell while the heat-capacity change for "acid" cells relative to the "neutral" cell is less well defined.

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