Thermodynamics of Standard Cells of the Saturated Cadmium Sulfate Type

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This paper gives data on the thermodynamic functions of standard cells of the saturated cadmium sulfate type, as obtained from calorimetric and equilibrium data at 25 °C or from the electromotive forces (emfs) and emf-temperature coefficients of the cell for the temperature range of 0 to 43.6 °C. The functions considered are the changes in Gibbs energy, enthalpy, entropy, and heat capacity for the cell reaction. The electromotive forces are expressed on the V_{69} volt and the t_{68} temperature scale. Results are expressed on the SI and for comparisons with literature data in terms of the defined thermochemical calorie. The effect of expressing the emf-temperature coefficient as a function of temperature in different ways on the values for the changes in entropy and heat capacity for the cell reaction is discussed. Finally, the observed emf of the standard cell at 25 °C is compared with emfs calculated from various values reported for the standard potentials of the cadmium-amalgam and mercury-mercurous sulfate electrodes and the activity coefficient of cadmium sulfate in saturated aqueous solution.

Key words: Emf-temperature coefficients of standard cells; emfs of standard cells; standard potential of standard cells; thermodynamics of standard cells.

1. Introduction

It is the purpose of this paper to present data on the thermodynamic functions of standard cells of the saturated cadmium sulfate type,[1] as obtained from calorimetric and chemical equilibrium data, and to compare these data with those obtained from the electromotive force (emf) and emf-temperature coefficient of the cell. The thermodynamic functions considered are the changes in Gibbs energy (free energy), ΔG; enthalpy (heat content), ΔH; entropy, ΔS; and heat capacity at constant pressure, ΔC_p, where the changes are equal to the differences between the thermodynamic quantities of the products and the reactants of the cell reaction. Thermodynamically, these are given or are related by:

$$\Delta G = \Delta H - T\Delta S = \Delta H + T[d(\Delta G)/dT]_p \quad (1)$$

$$\Delta S = \int_0^T \Delta C_p \, d \ln T \quad (2)$$

and

$$\Delta C_p = [d(\Delta H)/dT]_p \quad (3)$$

where T is the Kelvin temperature (defined in the thermodynamic scale by assigning 273.16 K to the triple point of water; freezing point of water, 273.15 K [1][2]).

The thermodynamic functions for a galvanic cell (or standard cell) may be obtained from its emf, E, and its emf-temperature coefficient, dE/dT, and are given by:

$$\Delta G = -nEF \quad (4)$$

$$\Delta H = -nEF + nFT(dE/dT) \quad (5)$$

$$\Delta S = nF(dE/dT) \quad (6)$$

and

$$\Delta C_p = nFT(d^2E/dT^2) \quad (7)$$

where n is the number of equivalents involved in the cell reaction (in the present case n is 2) and F is the Faraday. F has a value of 96487 coulombs per gram-equivalent [1, 2, 3, 4] or 23060.9 calories per volt per gram-equivalent.[3] Accordingly, a comparison may be made between the thermodynamics of the overall reaction of a standard cell as determined from calorimetric and chemical equilibrium data or from emf data.
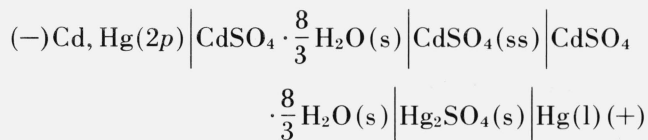
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2. The Standard Cell (saturated CdSO₄ type)

The conventional standard cell of the saturated cadmium sulfate type,[4] considered here, may be represented by:

$$(-)Cd, Hg(2p) \left| CdSO_4 \cdot \frac{8}{3} H_2O(s) \right| CdSO_4(ss) \left| CdSO_4 \right.$$
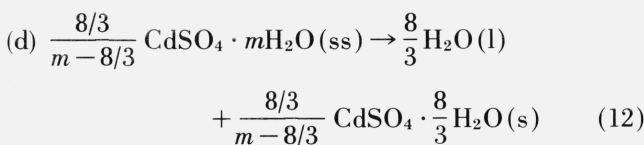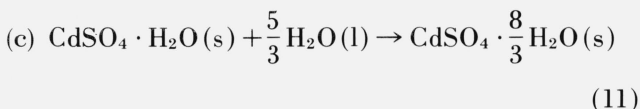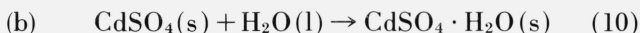$$\left. \cdot \frac{8}{3} H_2O(s) \right| Hg_2SO_4(s) \left| Hg(l) (+) \right.$$

where the vertical lines indicate the interface between two distinct phases (the amalgam consists of 2 phases, one solid and one liquid, but for simplicity vertical lines are not used in designating it), $2p = 2$ phases, ss = saturated solution, s = solid (or paste), and l = liquid. The cell reaction is [5]:

$$x Cd, y Hg(2p) + Hg_2SO_4(s) + \frac{8/3}{m - 8/3} CdSO_4$$
$$\cdot m H_2O(ss) \rightarrow \frac{m}{m - 8/3} CdSO_4 \qquad (8)$$
$$\cdot \frac{8}{3} H_2O(s) + 2Hg(l) + (x-1)Cd, y Hg(2p)$$
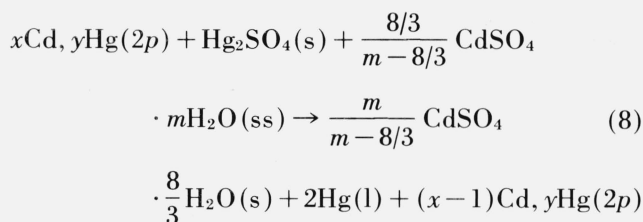
where x moles of Cd are associated with y moles of Hg in the amalgam and m is the number of moles of water associated with 1 mole of $CdSO_4$ in the saturated solution. Ten percent amalgams are now generally used, although there is now a trend to a return to the use of $12\frac{1}{2}$-percent amalgams as they are more suitable for portable (or shippable) cells. At 25 °C m has a value of 15.089 [6].

The overall reaction for the cell may be considered as the sum of five reactions, namely:

(a) $\quad Cd(s) + Hg_2SO_4(s) \rightarrow CdSO_4(s) + 2Hg(l) \qquad (9)$

(b) $\quad CdSO_4(s) + H_2O(l) \rightarrow CdSO_4 \cdot H_2O(s) \qquad (10)$

(c) $CdSO_4 \cdot H_2O(s) + \frac{5}{3} H_2O(l) \rightarrow CdSO_4 \cdot \frac{8}{3} H_2O(s)$

$$\qquad (11)$$

(d) $\frac{8/3}{m - 8/3} CdSO_4 \cdot m H_2O(ss) \rightarrow \frac{8}{3} H_2O(l)$

$$+ \frac{8/3}{m - 8/3} CdSO_4 \cdot \frac{8}{3} H_2O(s) \qquad (12)$$

and

(e) $\quad Cd(10\% \text{ amalgam}) \rightarrow Cd(s) \qquad (13)$

for which, reaction (e) excepted, calorimetric or thermal data are available.

3. Calorimetric and Chemical Equilibrium Data

Reaction (a)

For reaction (a) Cohen, Helderman, and Moesveld [7] obtained $-45,346$ cal mol^{-1} at 18 °C for the difference between the heats of formation of $CdSO_4$ and Hg_2SO_4; this difference is also equivalent to the heat of reaction (a) since the heats of formation of the elements, Cd and Hg, in their standard states are zero.[5] However, Cohen et al. arrived at their value for the heat of reaction (a) from combined calorimetric and emf data. They obtained their value by combining the value for the heat of solution of $CdSO_4$ in water at 18 °C to give a solution 2.559 percent in $CdSO_4$ with the value for the heat of reaction of an unsaturated standard cell (2.559% in $CdSO_4$) which they obtained from the observed emf of the cell at 18 °C and the measured emf-temperature coefficient of the cell at 18 °C.

For our purpose, however, we need to obtain the heat of reaction (a) directly from calorimetric data. This heat value may be obtained from the heats of reaction of Cd and $CdSO_4$ with other substances and of Hg and Hg_2SO_4 with other substances, as outlined by the following equations (unfortunately, most of the data were obtained many years ago). In these equations, the numbers in parentheses indicate, according to convention, the number of moles of water in which the substance is dissolved. Although, according to convention, the moles of water involved in dilution or solution [eqs (a4) and (a5) under Cd and $CdSO_4$, for example] are not included in representing the reaction they are included here so that the equations balance, but are shown in parentheses with an asterisk to indicate that the heat of formation of water is not used in determining the heat of dilution or solution. Likewise, when the water contains KI or $KI + I_2$, it is also shown in parentheses with a superscript to indicate that the heat of formation of this water, containing KI or $KI + I_2$, is not used in determining the heat of dilution or solution (in the summation of the following reactions this quantity cancels). Also, in each case the values reported in calories were first converted to international joules using the factor used by the individual authors; these were then converted to absolute joules using the factor 1.000167 and these in turn were then converted (for comparison purposes) to calories using the presently accepted thermochemical definition of the calorie (see footnote 3) and are designated by the symbol cf meaning conversion factor. Also in the equations that follow, s = solid, l = liquid, and g = gas. The numbers in parentheses after each value for ΔH denote the $\pm$ uncertainty, discussed later.
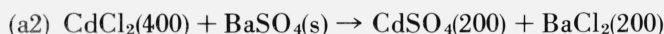
Cd and CdSO₄

(a1) $Cd(s) + 2 HCl(200) \rightarrow CdCl_2(400) + H_2(g)$

$\Delta H_1(20\ °C)$ $= -17,230(70)$ cal mol⁻¹ $= -72,033(293)$ J mol⁻¹ [8]
$\Delta H_1(18\ °C)$ $= -17,290(90)$ cal mol⁻¹ $= -72,284(377)$ J mol⁻¹ [8]
$\Delta H_1(18\ °C)^{cf}$ $= -17,276(90)$ cal mol⁻¹ $= -72,284(377)$ J mol⁻¹

(a2) $CdCl_2(400) + BaSO_4(s) \rightarrow CdSO_4(200) + BaCl_2(200)$

$\Delta H_2(19\ °C)$ $= 5,683(55)$ cal mol⁻¹ $= 23,742(230)$ J mol⁻¹ [9]
$\Delta H_2(18\ °C)$ $= 5,793(60)$ cal mol⁻¹ $= 24,201(251)$ J mol⁻¹ [10, 11]
$\Delta H_2(18\ °C)^{cf}$ $= 5,784(60)$ cal mol⁻¹ $= 24,201(251)$ J mol⁻¹

(a3) $BaCl_2(400) + H_2SO_4(400) \rightarrow BaSO_4(s) + 2 HCl(400)$

$\Delta H_3(19\ °C)$ $= -9,152(55)$ cal mol⁻¹ $= -38,234(230)$ J mol⁻¹ [9]
$\Delta H_3(18\ °C)$ $= -9,262(60)$ cal mol⁻¹ $= -38,694(251)$ J mol⁻¹ [10, 11]
$\Delta H_3(18\ °C)^{cf}$ $= -9,248(60)$ cal mol⁻¹ $= -38,694(251)$ J mol⁻¹

(a4) $BaCl_2(200) + (200\ H_2O)^* \rightarrow BaCl_2(400)$

$\Delta H_4(18\ °C)$ $= -50(1)$ cal mol⁻¹ $= -209(4)$ J mol⁻¹ [12]
$\Delta H_4(18\ °C)^{cf}$ $= -50(1)$ cal mol⁻¹ $= -209(4)$ J mol⁻¹

(a5) $2 HCl(400) \rightarrow 2 HCl(200) + (400\ H_2O)^*$

$\Delta H_5(18\ °C)$ $= 120(2)$ cal mol⁻¹ $= 502(8)$ J mol⁻¹ [12]
$\Delta H_5(18\ °C)^{cf}$ $= 120(2)$ cal mol⁻¹ $= 502(8)$ J mol⁻¹

(a6) $H_2SO_4(222) + (178\ H_2O)^* \rightarrow H_2SO_4(400)$

$\Delta H_6(18\ °C)$ $= -303(3)$ cal mol⁻¹ $= -1,268(12)$ J mol⁻¹ [12]
$\Delta H_6(18\ °C)^{cf}$ $= -303(3)$ cal mol⁻¹ $= -1,268(12)$ J mol⁻¹

(a7) $CdSO_4(400) \rightarrow CdSO_4(s) + (400\ H_2O)^*$

$\Delta H_7(18\ °C)$ $= 10,690(25)$ cal mol⁻¹ $= 44,756(105)$ J mol⁻¹ [7]
$\Delta H_7(18\ °C)^{cf}$ $= 10,697(25)$ cal mol⁻¹ $= 44,756(105)$ J mol⁻¹

(a8) $CdSO_4(200) + (200\ H_2O)^* \rightarrow CdSO_4(400)$

$\Delta H_8(18\ °C)$ $= -206(2)$ cal mol⁻¹ $= -862(8)$ J mol⁻¹ [12]
$\Delta H_8(18\ °C)^{cf}$ $= -206(2)$ cal mol⁻¹ $= -862(8)$ J mol⁻¹

sum: $Cd(s) + H_2SO_4(222) \rightarrow CdSO_4(s) + H_2(g) + (222\ H_2O)^*$

$\Delta H_{1-8}(18\ °C)^{cf} = -10,482(69)$ cal mol⁻¹ $= -43,858(289)$ J mol⁻¹

Hg and Hg₂SO₄

(a9) $Hg_2SO_4(s) + 2 KI(694)^\# \rightarrow Hg(l) + HgI_2(694)^\# + K_2SO_4(694)^\#$

\# — contains 5.25 moles of KI

$\Delta H_9(14\ °C)$ $= -44,100(560)$ cal mol⁻¹ $= -184,236(2339)$ J mol⁻¹ [13]

(a10) $HgI_2(858)^\phi \rightarrow Hg(l) + I_2(858)^\phi$
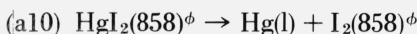
ϕ — contains 6.5 moles of KI and 1.0 mole of I_2

$\Delta H_{10}(14\ °C)$ $= 31,300(400)$ cal mol⁻¹ $= 130,762(1671)$ J mol⁻¹ [13]

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(a11) $I_2(858)^\phi \rightarrow I_2(s) + (858\ H_2O)^{\phi*}$
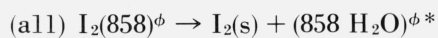
$\phi -$ contains 6.5 moles of KI and 1.0 mole of I_2

$\Delta H_{11}(14\ °C) = -200(2)$ cal mol^{-1} $= -835(8)$ J mol^{-1} [13]

sum of (a9), (a10), and (a11): $Hg_2SO_4(s) + 2\ KI(694)^\# + HgI_2(858) \rightarrow$
    $2\ Hg(l) + HgI_2(1123)^\alpha + K_2SO_4(1123)^\alpha + I_2(s)$
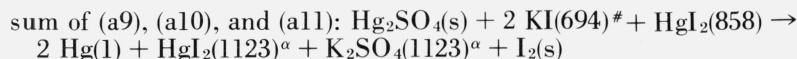
$\alpha -$ contains 8.5 moles of KI and 0.5 mole of I_2

$\Delta H_{9-11}(14\ °C) = -13,000(162)$ cal mol^{-1} $= -54,309(676)$ J mol^{-1}
$\Delta H_{9-11}(18\ °C) = -12,844(172)$ cal mol^{-1} $= -53,658(718)$ J mol^{-1} [10, 11, 14, 15]
$\Delta H_{9-11}(18\ °C)^{cf} = -12,825(172)$ cal mol^{-1} $= -53,658(720)$ J mol^{-1}

(a12) $HgI_2(1123)^\alpha \rightarrow HgI_2(858)^\phi + (265\ H_2O)^{\beta*}$

$\beta -$ contains 2 moles of KI

$\Delta H_{12}(18\ °C) = -2(0.1)$ cal mol^{-1} $= -8(0.4)$ J mol^{-1} [12]
$\Delta H_{12}(18\ °C)^{cf} = -2(0.1)$ cal mol^{-1} $= -8(0.4)$ J mol^{-1}

(a13) $Cl_2(g) + H_2(g) \rightarrow 2\ HCl(g)$
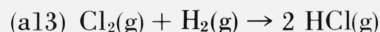
$\Delta H_{13}(18\ °C) = -44.120(24)$ cal mol^{-1} $= -184.644(100)$ J mol^{-1} [16]
$\Delta H_{13}(18\ °C)^{cf} = -44,131(24)$ cal mol^{-1} $= -184,644(100)$ J mol^{-1}

(a14) $I_2(s) + 2\ HCl(g) \rightarrow 2\ HI(g) + Cl_2(g)$
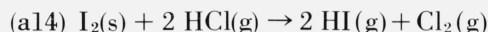
$\Delta H_{14}(22\ °C) = 55.933(100)$ cal mol^{-1} $= 233,985(418)$ J mol^{-1} [17]
$\Delta H_{14}(18\ °C) = 55,949(110)$ cal mol^{-1} $= 234,053(460)$ J mol^{-1} [10, 18]
$\Delta H_{14}(18\ °C)^{cf} = 55,940(110)$ cal mol^{-1} $= 234,053(460)$ J mol^{-1}

(a15) $2\ HI(g) + (222\ H_2O)^* \rightarrow 2\ HI(111)$

$\Delta H_{15}(18\ °C) = -38,344(50)$ cal mol^{-1} $= -160,431(209)$ J mol^{-1} [12]
$\Delta H_{15}(18\ °C)^{cf} = -38,344(50)$ cal mol^{-1} $= -160,431(209)$ J mol^{-1}

(a16) $2\ HI(100) + 2\ KOH(100) \rightarrow 2\ KI(200) + 2\ H_2O(l)$
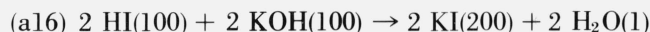
$\Delta H_{16}(20\ °C) = -27,830(20)$ cal mol^{-1} $= -116,349(84)$ J mol^{-1} [19]
$\Delta H_{16}(18\ °C) = -28,034(29)$ cal mol^{-1} $= -117,202(121)$ J mol^{-1} [19]
$\Delta H_{16}(18\ °C)^{cf} = -28,012(29)$ cal mol^{-1} $= -117,202(121)$ J mol^{-1}

(a17) $2\ KOH(111) + 2\ HI(111) + 2\ KI(200) \rightarrow 2\ KOH(100) + 2\ HI(100) + 2\ KI(222)$

$\Delta H_{17}(18\ °C) = 16(1)$ cal mol^{-1} $= 67(4)$ J mol^{-1} [12]
$\Delta H_{17}(18\ °C)^{cf} = 16(1)$ cal mol^{-1} $= 67(4)$ J mol^{-1}

(a18) $2\ KI(222) + (944\ H_2O)^{\gamma*} \rightarrow 2\ KI(694)^\#$

$\gamma -$ contains 10.5 moles of KI

$\Delta H_{18}(18\ °C) = 115(1)$ cal mol^{-1} $= 481(4)$ J mol^{-1} [12]
$\Delta H_{18}(18\ °C)^{cf} = 115(1)$ cal mol^{-1} $= 481(4)$ J mol^{-1}

(a19) $K_2SO_4(277.5) + 2\ H_2O(l) \rightarrow H_2SO_4(55.5) + 2\ KOH(111)$
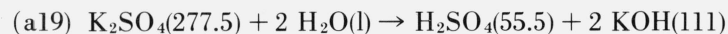
$\Delta H_{19}(17\ °C) = 32,966(300)$ cal mol^{-1} $= 137,930(1255)$ J mol^{-1} [20]
$\Delta H_{19}(18\ °C) = 32,907(310)$ cal mol^{-1} $= 137,683(1297)$ J mol^{-1} [10, 14, 15]
$\Delta H_{19}(18\ °C)^{cf} = 32,907(310)$ cal mol^{-1} $= 137,683(1297)$ J mol^{-1}

(a20) $H_2SO_4(55.5) + (166.5\ H_2O)^* \rightarrow H_2SO_4(222)$

$\Delta H_{20}(18\ °C) \quad = -390(10)$ cal mol^{-1} $= -1{,}632(42)$ J mol^{-1} [12]

$\Delta H_{20}(18\ °C)^{cf} = -390(10)$ cal mol^{-1} $= -1{,}632(42)$ J mol^{-1}

(a21) $K_2SO_4(1123) \rightarrow K_2SO_4(277.5) + (845.5\ H_2O)^{\delta *}$

$\delta -$ contains 8.5 moles of KI

$\Delta H_{21}(18\ °C) \quad = -195(2)$ cal mol^{-1} $= -816(8)$ J mol^{-1} [12]

$\Delta H_{21}(18\ °C)^{cf} = -195(2)$ cal mol^{-1} $= -816(8)$ J mol^{-1}

sum: $Hg_2SO_4(s) + H_2(g) + (222\ H_2O)^* \rightarrow 2\ Hg(l) + H_2SO_4(222)$
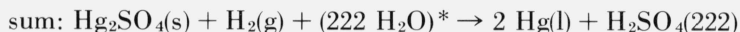
$\Delta H_{9-21}(18\ °C)^{cf} = -34{,}921(135)$ cal mol^{-1} $= -146{,}109(565)$ J mol^{-1}

Cd, CdSO$_4$ − Hg$_2$SO$_4$, Hg

sum: $Cd(s) + Hg_2SO_4(s) \rightarrow CdSO_4(s) + 2\ Hg(l)$
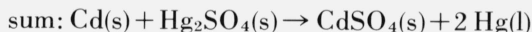
$\Delta H_{1-21}(18\ °C)^{cf} = -45{,}403(66)$ cal mol^{-1} $= -189{,}967(276)$ J mol^{-1}
$\qquad\qquad\qquad = -45{,}403(397)$ cal mol^{-1} $= -189{,}967(1661)$ J mol^{-1}

It should be noted here that two uncertainties are given; these are discussed later under overall uncertainties. This value for $\Delta H_{1-21}(18\ °C)^{cf}$ may be converted to a value at 25 °C by using known values of the heat capacities of Cd(s) [10], Hg$_2$SO$_4$(s) [14], CdSO$_4$(s) [21, 22] and Hg(l) [14], as a function of temperature, namely[6]:

$C_p[Cd(s)] \qquad = (5.333\ +0.00294\ T)$ cal mol^{-1} (14)

$C_p[Hg_2SO_4(s)] \quad = (13.8\ +0.060\ T)$ cal mol^{-1} (15)

$C_p[CdSO_4(s)] \quad = (10.771 + 0.0437\ T)$ cal mol^{-1} (16)

$C_p[Hg(l)] \qquad = (7.368\ -0.0023\ T)$ cal mol^{-1} (17)

$\Delta C_p[\text{reaction (a)}] = (6.374\ -0.02384\ T)$ cal mol^{-1} (18)

all of which may be expressed in J mol^{-1} using the relation given in footnote 3. The heat of reaction (a) at 25 °C is then found to be $-45{,}407$ cal mol^{-1} or $-189{,}983$ J mol^{-1}. Incidentally, the data of Bichowsky and Rossini [12] for the overall reaction lead to $-45{,}720$ cal mol^{-1} at 18 °C or $-45{,}716$ cal mol^{-1} at 25 °C (on the presently accepted definition of the calorie) for ΔH for reaction (a); NBS Circular 500 [23] gives $-44{,}021$ cal mol^{-1} at 25 °C while revised NBS Circular [24] gives $-45{,}450$ cal mol^{-1}; this last value agrees within 43 cal mol^{-1} of the overall sum given above. These latter values [12, 23, 24] are combinations of heat and emf data.

Notes on some of the above reactions should be given here. Richards and Tamaru [8] found that the temperature coefficient of the heat of solution of cadmium in concentrated HCl was -71 cal/°C and believed that even for dilute acid it amounted to as much as -30 cal/°C. Since reaction (a1) is for dilute

acid -30 cal/°C is taken for the temperature coefficient; owing to the estimation made by Richards and Tamaru a large uncertainty of ± 10 cal/°C is attributed to this value.

Thomsen [9] stated that the temperature of his observations for reactions (a2) and (a3) was 18–20 °C. A mean temperature of 19 °C is taken here, and Thomsen's values were corrected to 18 °C using the known heat capacity of BaSO$_4$(s) [10] as a function of temperature and the heat capacities of the Ba^{++} and SO$_4^{=}$ ions at 25 °C given by Pitzer and Brewer [11] (these latter values were assumed to be temperature and concentration independent). Since the difference of (a2) and (a3) is taken in arriving at the value for the overall reaction, an error in this temperature correction is negligible.

The temperature correction for the sum of the reactions (a9), (a10), and (a11) was obtained from the known heat capacities of Hg$_2$SO$_4$(s) [14], Hg(l) [14], and I$_2$(s) [10] as functions of temperature and of KI, HgI$_2$, and K$_2$SO$_4$ as functions of concentration and temperature as follows. The heat capacity of HgI$_2$ was taken equal to that of KI (since it was dissolved in KI solutions) and that of K$_2$SO$_4$ as equal to 0.917 times twice the heat capacity of KOH (the temperature coefficient for K$_2$SO$_4$ was taken equal to that for KOH). The factor 0.917 is the ratio of the heat capacity of 2KOH and K$_2$SO$_4$ at infinite dilution; the value for SO$_4^{=}$ was taken from the compilation of Pitzer and Brewer [11]. The heat capacities of aqueous solutions of KI and KOH at 25 °C, as a function of concentration, were taken from the compilation of Parker [15]. The temperature coefficient for HCl was used for the temperature coefficient of KI and the temperature coefficient of NaOH was used for the temperature coefficient for KOH [15]. These values lead to:

$\Delta C_p[\text{sum of reactions (a9), (a10), (a11)}]$

$= -579.9 + 2.14\ T$ (19)

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[6] Each equation was altered slightly to make it conform with the values in reference [24] at 25 °C.

for the change in heat capacity for the sum of reactions (a9), (a10), and (a11). The estimated uncertainty for equation (19) is ± 10 cal/°C.

The temperature correction for reaction (a14) was obtained using the known heat capacities of $I_2(s)$ [10], HCl(g) [18], HI(g) [18], and $Cl_2(g)$ [10] as functions of temperature, or:

$$\Delta C_p \text{ [reaction (a14)]} = -0.84 - 0.0101\,T - 76000/T^2 \quad (20)$$

An uncertainty of ± 10 cal/°C is assigned to this temperature correction.

Richards and Rowe [19] found an average of -50.9 cal/°C for the temperature coefficient for the neutralization of HCl(100) and of $HNO_3(100)$ with LiOH(100), NaOH(100), and KOH(100). This average temperature coefficient is assumed here to also apply to the neutralization of KOH(100) with HI(100) with an uncertainty of ± 9 cal/°C, the spread found between the values found for the neutralization of HCl(100) and of HNO_3 (100) with KOH(100).

Müller [20] measured the neutralization of H_2SO_4 (55.5) with potassium hydroxide of various dilutions (one mole of KOH in 13.508, 27.420, and 51.626 liters of water) at 17 °C. A value for the heat of neutralization of $H_2SO_4(55.5)$ with one mole of KOH in 2 liters of water was obtained by extrapolation of ΔH (neutralization) against $\sqrt{\text{volume}}$; ΔH (neutralization) versus $\sqrt{\text{volume}}$ is a straight line over the range of observations made by Müller. An uncertainty of ± 150 cal/°C per mole of KOH(111) is assigned to this heat of reaction owing to the spread in the three values obtained by Müller. This neutralization value is much higher than the older values of Thomsen [9] and Berthelot [25]. The older values were probably low because of the presence of carbonate in the alkali as has been shown for similar cases by Keyes, Gillespie, and Mitsukuri [26]. The value was corrected to 18 °C, with an estimated additional uncertainty of ± 10 cal/°C using the known heat capacity of water [14][7] as a function of temperature and of H_2SO_4. KOH, and K_2SO_4 as functions of concentration and temperature using the procedure discussed above in obtaining the temperature coefficient for the sum of the reactions (a9), (a10), and (a11). These values lead to

$$\Delta C_p \text{ [(reaction (a19)]} = 574.17 - 1.772\,T \quad (21)$$

for the change in heat capacity for reaction (a19).

For the reactions (a13) and (a14) the uncertainties given in the parentheses are the $\pm$ uncertainties given by the experimenters. In the other cases the experimenters were not explicit on their experimental uncertainties. For (a1), Richards and Tamaru [8] stated that the maximum uncertainty if all errors were additive, which would be highly unlikely, would be 70 cal mol⁻¹, and that the probable error was undoubtedly much less. Their maximum uncertainty is retained

here and an additional uncertainty of ± 10 cal/°C is assigned to the temperature coefficient. The uncertainties assigned to (a2) and (a3) were deduced from the temperature correction, i.e., were taken as one half the correction. For (a7), Cohen, Helderman and Moesveld [7] made eight determinations of the heat evolved; the standard deviation of their mean value is 7 cal mol⁻¹. The average spread in their values is taken, however, as the overall uncertainty. For (a10) Varet gave a general value which differs from that given above for (a10) by 400 cal mol⁻¹; this is taken as the uncertainty and the same percentage uncertainty is assigned to (a9), a reaction also studied by Varet. For (a16) Richards and Rowe stated that the maximum uncertainty in their value was 0.07 percent, and is used here. The estimated uncertainty for (a19) was discussed above. The uncertainties for the other reactions, which are mostly ones for solution or dilution, are estimated ones.

The overall uncertainty value is obtained from the sum of the uncertainties for each reaction taking care of sign. An overall uncertainty may also be taken as the root sum square value of the uncertainties of the 21 reactions, namely 397 cal mol⁻¹ or 1661 J mol⁻¹ and is the second uncertainty given above. The actual uncertainty probably lies between these two estimates. A root mean square value of the uncertainty is 88 cal mol⁻¹ or 368 J mol⁻¹; this value of the uncertainty is close to the first one listed above.

Values for the entropy of Cd(s), $Hg_2SO_4(s)$, $CdSO_4(s)$, and Hg(l) at 25 °C are 12.37 [27], 47.96 [24], 29.41 [21], and 18.19 [27] cal K⁻¹ mol⁻¹, or 51.75, 200.66, 123.05, and 76.02 J K⁻¹ mol⁻¹, respectively. Therefore, ΔS_a for reaction (a) is 5.42 cal K⁻¹ mol⁻¹ or 22.68 J K⁻¹ mol⁻¹. This value combined with the value of ΔH_a, given above, gives according to eq (1) $-47,023$ cal mol⁻¹ or $-196,745$ J mol⁻¹ for the Gibbs energy (free energy) change, ΔG_a, for reaction (a). Since $\Delta G = -nEF$ [see eq (4)] E would be 1.0195396 V at 25 °C for the standard cell of the saturated cadmium sulfate type, if the cell reaction were as depicted by reaction (a). Also, since $\Delta S = nF(dE/dT)$ [see eq (6)], dE/dT for the cell at 25 °C would be 0.00011751 V/°C, if the cell reaction were as depicted by reaction (a). Since these values do not agree with the observed ones (see later) it follows that the cell reaction does not correspond to reaction (a).

The heat capacities at 25 °C of Cd(s), $Hg_2SO_4(s)$, $CdSO_4(s)$, and Hg(l) are, respectively, 6.21 [24], 31.54 [24], 23.806 [24], and 6.688 [24] cal K⁻¹ mol⁻¹ or 25.90, 132.00, 99.62, and 27.82 J K⁻¹ mol⁻¹; ΔC_p is therefore, -0.580 cal K⁻¹ mol⁻¹ or -2.427 J K⁻¹ mol⁻¹. Stull and Sinke [27] give 6.19 cal K⁻¹ mol⁻¹ for Cd(s). Papadopoulos and Giauque [21] give 23.806 cal K⁻¹ mol⁻¹ for $CdSO_4(s)$, and Giauque, Barieau and Kunzler [14] give 31.689 and 6.702 cal K⁻¹ mol⁻¹ for $Hg_2SO_4(s)$ and Hg(l), respectively. These values yield -0.669 cal K⁻¹ mol⁻¹ or -2.799 J K⁻¹ mol⁻¹ for $\Delta C_p(a)$.

Reaction (b)

The Gibbs energy change for reaction (b) is given by:

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[7] Equation given in reference [14] was altered slightly to make equation consistent with the 25 °C value given in reference [22].

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$$\Delta G_b = RT \ln \frac{p^*}{p^0} = RT \ln \frac{0.62}{23.7667}$$

$$= -2160 \text{ cal mol}^{-1} = -9037 \text{ J mol}^{-1} \quad (22)$$

where p^0 is the vapor pressure of water at 25 °C [28], p^* the vapor pressure of the system $CdSO_4 \cdot H_2O - H_2O$, T the Kelvin temperature, and R the gas constant (1.98717 cal K^{-1} mol^{-1} or 8.3143 J K^{-1} mol^{-1} [1]). Ishikawa and Murooka [29] obtained 0.62 mm Hg for p^*. The values in mm Hg may be converted to pascals by the relation 1 mm Hg (0 °C) = 1.333224 $\times 10^2$ pascals.

The entropies for $CdSO_4(s)$, $H_2O(l)$, and $CdSO_4 \cdot H_2O(s)$ at 25 °C are, respectively, 29.41 [21], 16.71 [24], and 36.82 [21] cal K^{-1} mol^{-1} or 123.05, 69.91, 154.05 J K^{-1} mol^{-1}; therefore, ΔS_b for reaction (b) is -9.30 cal K^{-1} mol^{-1} or -38.91 J K^{-1} mol^{-1}. This value combined with the value for ΔG_b above gives by eq (1) $-4,933$ cal mol^{-1} or $-20,640$ J mol^{-1} for ΔH_b, the heat of reaction for reaction (b). Papadopoulos and Giauque [21] measured the heats of solution of $CdSO_4(s)$ and $CdSO_4 \cdot H_2O(s)$ in 400 moles of water at 25 °C for which they obtained $-10,977$ and -6095 cal mol^{-1} or -45.928 and -25.501 J mol^{-1}, respectively. These yield $-4,882$ cal mol^{-1} or $-20,426$ J mol^{-1} for ΔH_b which differs by 51 cal mol^{-1} or 214 J mol^{-1} from that calculated above.

The heat capacities of $CdSO_4(s)$, $H_2O(l)$, and $CdSO_4 \cdot H_2O(s)$ at 25 °C are, respectively, 23.806 [21], 17.995 [30], and 32.157 [21] cal K^{-1} mol^{-1} or 99.58, 75.29, and 134.544 J K^{-1} mol^{-1}; therefore, $\Delta C_{p(b)}$ for reaction (b) is -9.644 cal K^{-1} mol^{-1} or -40.350 J K^{-1} mol^{-1}.

Reaction (c)

The Gibbs energy change for reaction (c) is given by:

$$\Delta G_c = \frac{5}{3} RT \ln \frac{p^{**}}{p^0} = \frac{5}{3} RT \ln \frac{17.4}{23.7667}$$

$$= -308 \text{ cal} = -1289 \text{ J} \quad (23)$$

where p^{**} is the vapor pressure of the system $CdSO_4 \cdot \frac{8}{3} H_2O - CdSO_4 \cdot H_2O$ and p^0, T, and R have the same significance as given above. The average of the results of Ishikawa and Murooka [29] and of Carpenter and Jette [31] gives 17.4 mm Hg for p^{**}. Conversion to pascals may be done as stated above.

The entropies for $CdSO_4 \cdot H_2O(s)$ and $H_2O(l)$ have been given above. The entropy of $CdSO_4 \cdot \frac{8}{3} H_2O(s)$ is 54.89 [21] cal K^{-1} mol^{-1} or 229.66 J K^{-1} mol^{-1}. ΔS_c is, therefore, -9.78 cal K^{-1} mol^{-1} or -40.92 J K^{-1} mol^{-1}. This value combined with the value for ΔG_c given above gives by eq (1) $-3,224$ cal or $-13,489$ J for ΔH_c, the heat of reaction for reaction (c). Papadopoulos and Giauque [21] measured the heats of solution of $CdSO_4 \cdot H_2O(s)$ and $CdSO_4 \cdot \frac{8}{3} H_2O(s)$ in 400 moles of water at 25 °C for which they obtained $-6,095$ and

$-2,899$ cal mol^{-1} or $-25,502$ and $-12,129$ J mol^{-1}, respectively. These yield $-3,196$ cal mol^{-1} or $-13,372$ J mol^{-1} for ΔH_c which differs by 28 cal mol^{-1} or 117 J mol^{-1} from that calculated above.

The heat capacities of $CdSO_4 \cdot H_2O(s)$ and $H_2O(l)$ have been given above. The heat capacity of $CdSO_4 \cdot \frac{8}{3} H_2O(s)$ at 25 °C is 50.972 cal K^{-1} mol^{-1} [21] or 213.26 J K^{-1} mol^{-1}. Therefore, $\Delta C_{p(c)}$ for reaction (c) is -11.177 cal or -46.765 J.

Reaction (d)

The Gibbs energy change for reaction (d) is given by:

$$\Delta G_d = \frac{8}{3} RT \ln \frac{p^0}{p^s} = \frac{8}{3} RT \ln \frac{23.7667}{21.17} = 184 \text{ cal} = 770 \text{ J} \quad (24)$$

where p^s is the vapor pressure of a saturated solution of $CdSO_4 \cdot \frac{8}{3} H_2O$ and p^0, T, and R have the significance given above. Ishikawa and Murooka [29] obtained 21.17 mm Hg for the vapor pressure of the saturated solution at 25 °C; this value may be converted to pascals as described above. Holsboer [32] found that 1,044 calories or 4,368 joules of heat were evolved when one mole of $CdSO_4 \cdot \frac{8}{3} H_2O(s)$ was dissolved in enough water to form the saturated solution at 25 °C; for $(8/3)/(m-8/3)$ mole of salt the heat evolved would be 224 cal or 938 J since $m = 15.089$ [5, 6] at 25 °C and $(8/3)/(m-8/3) = 0.2147$. Combining these values for ΔG_d and ΔH_d gives 0.13 cal K^{-1} or 0.544 J K^{-1} for ΔS_d, the entropy change for reaction (d).

Cohen and Moesveld [33] obtained 0.5836 cal g^{-1} or 2.4414 J g^{-1} for the specific heat of a saturated solution of $CdSO_4 \cdot \frac{8}{3} H_2O$ at 19 °C which becomes 0.5823 cal g^{-1} or 2.4359 J g^{-1} at 25 °C based on the higher concentration of the saturated solution at 25 °C and the ratio of the specific heat of water at 25 and 19 °C. Accordingly $(8/3)/(m-8/3)$ mole of a saturated solution of $CdSO_4 \cdot \frac{8}{3} H_2O$ has a heat capacity of 59.93 cal K^{-1} or 250.705 J K^{-1} at 25 °C; on the present thermochemical calorie the value is 59.92 cal K^{-1} or 250.706 J K^{-1}. Combining this value with the heat capacity of $H_2O(l)$ and $CdSO_4 \cdot \frac{8}{3} H_2O(s)$, given above, gives -0.999 cal K^{-1} or -4.180 J K^{-1} for $\Delta C_{p(d)}$ for reaction (d).

The above values are summarized in tables 1 and 2; data are given in SI units in the first section of each table and in defined calories in the second section. Table 1 is based on experimental values for the Gibbs energy changes for reactions (b), (c), and (d) and the enthalpy changes for reactions (a) and (d). Table 2 is based on experimental values for the Gibbs energy change of reaction (d) and the enthalpy changes of reactions (a), (b), (c), and (d). The addition of these values for reactions (a), (b), (c), and (d) gives sum 1 or the values for the reaction in a standard cell of the

TABLE 1. *Thermodynamic data for the reaction in standard cells of the saturated cadmium sulfate type at 25 °C—based on experimental Gibbs energies for reactions (b), (c), and (d) and experimental enthalpies for reactions (a) and (d)*

Reaction	Gibbs energy change ΔG J mol⁻¹	Enthalpy change ΔH J mol⁻¹	Entropy change ΔS J K⁻¹ mol⁻¹	Heat-capacity change ΔC_p J K⁻¹ mol⁻¹
(a)............	#(−196,745)	−189,983	22.68	φ−2.427
(b)............	−9,037	(−20,640)	−38.91	−40.350
(c)............	−1,289	(−13,489)	−40.92	−46.765
(d)............	770	937	(0.544)	−4.180
sum 1.......	−206,301	−223,175	−56.606	−93.722
(e)*	9,743	23,764	47.03	0
sum 2^p.....	−196,558	−199,411	−9.576	−93.722
(e)**........	9,738	21,240	38.58	204.26
sum 3^q......	−196,563	−201,935	−18.026	110.538
	(cal mol⁻¹)^j	cal mol⁻¹	cal K⁻¹ mol⁻¹	cal K⁻¹ mol⁻¹
(a)............	(−47,023)	−45,407	5.42	φ−0.580
(b)............	−2,160	(−4,933)	−9.30	−9.644
(c)............	−308	(−3,224)	−9.78	−11.177
(d)............	184	224	(0.13)	−0.999
sum 1.......	−49,307	−53,340	−13.53	−22.400
(e)*.......	2,328.6	5,679.8	11.24	0
sum 2^p.....	−46,978.4	−47,660.2	−2.29	−22.400
(e)**........	2,327.5	5,076.4	9.22	48.82
sum 3^q.....	−46,979.5	−48,263.6	−4.31	26.420

TABLE 2. *Thermodynamic data for the reaction in standard cells of the saturated cadmium sulfate type at 25 °C—based on experimental enthalpies for reactions (a), (b), (c), and (d) and experimental Gibbs energy for reaction (d)*

Reaction	Gibbs energy change ΔG J mol⁻¹	Enthalpy change ΔH J mol⁻¹	Entropy change ΔS J K⁻¹ mol⁻¹	Heat-capacity change ΔC_p J K⁻¹ mol⁻¹
(a)............	#(−196,745)	−189,983	22.68	φ−2.402
(b)............	(−8,824)	−20,426	−38.91	−40.350
(c)............	(−1,171)	−13,372	−40.92	−46.765
(d)............	770	937	(0.544)	−4.180
sum 1.......	−205,970	−222,844	−56.606	−93.722
(e)*..........	9,743	23,764	47.03	0
sum 2^p.....	−196,227	−199,080	−9.576	−93.722
(e)**........	9,738	21,240	38.58	204.26
sum 3^q.....	−196,232	−201,604	−18.026	110.538
	(cal mol⁻¹)^j	cal mol⁻¹	cal K⁻¹ mol⁻¹	cal K⁻¹ mol⁻¹
(a)............	(−47,023)	−45,407	5.42	φ−0.580
(b)............	(−2,109)	−4,882	−9.30	−9.644
(c)............	(−280)	−3,196	−9.78	−11.177
(d)............	184	224	(0.13)	−0.999
sum 1.......	−49,228	−53,261	−13.53	−22.400
(e)*.........	2,328.6	5,679.8	11.24	0
sum 2^p.....	−46,899.4	−47,581.2	−2.29	−22.400
(e)**........	2,327.5	5,076.4	9.22	48.82
sum 3^q......	−46,900.5	−48,184.6	−4.31	26.420

\# Values in parentheses were calculated from the relation $\Delta G = \Delta H - T\Delta S$.
φ See text for alternate value of −2.799 J K⁻¹ mol⁻¹ or −0.669 cal K⁻¹ mol⁻¹.
* Based on data of Hulett [34] and Getman [35].
^{p} Sum 1 + (e)*.
** Based on data of Parks and LaMer [39].
^{q} Sum 1 + (e)**.
^{j} 1 Thermochemical calorie (defined) = 4.184 J [1].

saturated cadmium sulfate type at 25 °C if the anode were made of cadmium metal rather than cadmium amalgam.

Reaction (e)

Calorimetric and chemical equilibrium measurements on reaction (e) have not been made. It is necessary, therefore, to rely on electrochemical measurements for information on reaction (e). Hulett [34] and Getman [35] measured the emf of the cell:

$$(-)\,Cd(metal)\,|\,CdSO_4(sol)\,|\,Cd\,amalgam\,(8-10\%)(+) \quad (A)$$

at a series of temperatures and obtained:

$$E\text{ (in volts)} = 0.050487 - 0.0002437\,(t - 25\ °C) \quad (25)$$

for the emf as a function of temperature. In cell (A) sol denotes an aqueous solution. Sir Frank Smith [36] showed that 8-percent and 10-percent amalgams have

the same electrical potential. Hulett and Getman's emfs, expressed in international volts were converted to absolute volts here using the relation: 1 international volt (USA) = 1.0003384 absolute volts [37, 38]. Their results give 2,328.6 cal mol⁻¹, 5,679.8 cal mol⁻¹, 11.24 cal K⁻¹ mol⁻¹, and 0 cal K⁻¹ mol⁻¹ or 9,742.9 J mol⁻¹, 23,764.2 J mol⁻¹, 47.03 J K⁻¹ mol⁻¹, and 0 J K⁻¹ mol⁻¹ for ΔG_e, ΔH_e, ΔS_e, and $\Delta C_{p(e)}$, respectively, for reaction (e). (Note that reaction (e) is for the reverse reaction of the above cell.) These values are added to sum 1 in tables 1 and 2 to give sum 2 for the thermodynamic data for the reaction at 25 °C in standard cells of the saturated cadmium sulfate type.

Parks and LaMer [39] also measured the emf of the above cell (A) over the temperature range of 0 to 40 °C. They expressed their results by the equation:

$$E\text{ (in volts)} = 0.055399 - 0.000148\,t - 0.00000385\,t^2 + 0.000000075\,t^3. \quad (26)$$

Their emfs, given in international volts were converted to

here to absolute volts using the relation given directly above. Their results lead to 2,327.5 cal mol^{-1}, 5.076.4 cal mol^{-1}, 9,22 cal K^{-1} mol^{-1}, and 48.82 cal K^{-1} mol^{-1} or 9.738.3 J mol^{-1}, 21.239.6 J mol, 38.58 J K^{-1} mol^{-1}, and 204.26 J K^{-1} mol^{-1} for ΔG_e, ΔH_e, ΔS_e, and $\Delta C_{p(e)}$, respectively, for reaction (e) at 25 °C. The value for ΔG_e agrees well with that obtained from Hulett and Getman's data but the values for the other thermodynamic functions do not. These differences are discussed in more detail later. These values are added to sum 1 in tables 1 and 2 give sum 3 for alternate thermodynamic data for the reaction at 25 °C in standard cells of the saturated cadmium sulfate type.

4. Electromotive Force and Emf-temperature Coefficient

The electromotive force of the so-called "neutral" or Normal standard cell was initially determined at 20 °C in terms of the international ohm and the international ampere by an International Committee on Electrical Units and Standards which met at the National Bureau of Standards in 1910.[8] As a result of numerous experiments they arrived at a value of 1.0183 V for the emf of the cell at 20 °C; values derived from this were later assumed to be significant to the fifth, sixth, or seventh decimal as a basis of measurement [5] and subsequent "absolute" measurements of the ohm and ampere confirmed the validity of this process. Somewhat earlier [42, 43, 44] Wolff investigated extensively the emf-temperature coefficient of the "neutral" type of standard cell made with 12½-percent cadmium amalgams. Wolff based his emf-temperature formula (or equation) on the results obtained from 0 to 40 °C, inclusive, on 137 cells, made in various ways, after rejecting the results on 63 cells for a variety of reasons, including cell leakage, abnormal initial emfs, excessive emf-temperature hysteresis, erratic behavior, or chemical instability. Wolff [42] first arrived at the approximate emf-temperature formula:

$$E_t = E_{20\,°C} - 0.0000406(t-20) - 0.000000939(t-20)^2 + 0.000000009(t-20)^3 \quad (27)$$

by the method of least squares on the means of all observations on ten cells selected on the basis of their fast attainment of equilibrium after temperature changes. Using this approximate equation he then determined the residuals for all of the 137 cells at each temperature and calculated the corrections needed for the coefficients in eq (27) above. In this way he arrived at the emf-temperature formula:

$$E_t = E_{20\,°C} - 0.00004064(t-20) - 0.000000942(t-20)^2 + 0.0000000096(t-20)^3 \quad (28)$$

The 137 cells used to obtain eq (28) consisted of seven different groups of cells, namely, (1) 11 cells made with electrolytic mercurous sulfate prepared at low current densities [45], (2) 53 cells made with electrolytic mercurous sulfate prepared at higher current densities [46], (3) 22 cells made with mercurous sulfate prepared chemically in different ways, (4) 19 cells made with various samples of commercial mercurous sulfate, (5) 13 cells made with exchange (gift) samples of electrolytic mercurous sulfate, (6) nine exchange cells (foreign and domestic), and (7) 10 cells made with high current-density electrolytic mercurous sulfate but with different samples of cadmium sulfate synthesized or treated in various ways. Except for group (7) the cadmium sulfate was commercial grade which was recrystallized several times from distilled water.

Wolff [43] later gave a different formula wherein the first, second, and third coefficients in eq (27) or (28) were, respectively, 0.00004075, −0.000000944, and 0.0000000098 (these were uncorrected for residuals, compare data in references [42] and [43]).

The International Conference on Electrical Units and Standards meeting in London in 1908 adopted the formula (since known as the International formula) [47]:

$$E_t = E_{20\,°C} - 0.0000406(t-20) - 0.00000095(t-20)^2 + 0.00000001(t-20)^3 \quad (29)$$

giving weight to Wolff's original (provisional) emf-temperature formula, eq (27) above. It should be noted that practically the same result follows if the data obtained on groups (4) and (6), for which the cells were not well characterized, and on those cells for which the emf-temperature coefficient at 20 °C exceeds one microvolt are eliminated; these eliminations leave 99 cells for evaluation. Using these 99 cells gives:

$$E_t = E_{20\,°C} - 0.00004049(t-20) - 0.000000951(t-20)^2 + 0.00000000962(t-20)^3 \quad (30)$$

Equation (29), the International Temperature Formula, has been confirmed within the experimental uncertainty many times in succeeding years [48–53] for temperatures from 15 to 40 °C. The limits of uncertainty in the equation are discussed later.

Equations (29) and (30) may be given in the alternate forms:

$$E = E_{0\,°C} + 0.0000094\,t - 0.00000155\,t^2 + 0.00000001\,t^3 \quad (31)$$

$$E = E_{0\,°C} + 0.000009094\,t - 0.0000015282\,t^2 + 0.00000000962\,t^3. \quad (32)$$

Vigoureux and Watts [54], Obata and Ishibashi [55], and Ishibashi and Ishizaki [50] also measured the emf-temperature coefficient of standard cells of the saturated cadmium sulfate type. However, their cells were of the "acid" type. i.e., sulfuric acid was added to the cell in small amounts (0.1 N for ref. [54] and various amounts for ref. [55] and ref. [50]) and will, therefore, not be considered here. Furthermore, Vigoureux and Watts gave emphasis to measurements below 0 °C.

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[8] Some measurements on the emf of standard cells were made earlier (see references [5, 40], and [41]) but these were not standardized internationally in terms of the mechanical units. The term "neutral" cell refers to one in which sulfuric acid, in low concentrations, is not intentionally added to the cell; actually, cadmium sulfate hydrolyzes to give sulfuric acid of 0.00092 N [5].

Obata and Ishibashi made measurements only from 15.6 to 29.6 °C, and Ishibashi and Ishizaki from 15 to 30 °C.

The results of Wolff were expressed in international volts and on the temperature scale based on the constant-volume hydrogen gas thermometer, defined in terms of melting ice (0 °C) and boiling water (100 °C), the hydrogen being taken at an initial manometric pressure of one meter of mercury; realization of the temperature scale was effected through mercurial thermometers calibrated in terms of the gas thermometer [56]. This temperature scale was the same as that adopted as the International Temperature Scale of 1927 [57].

On January 1, 1948 the international volt was replaced by the absolute volt; the change [37] for the United States was 1 international volt (USA) = 1.000330 absolute volts. Then on January 1, 1969 another change [38] was made; the factor was: 1 USA volt$_{48}$ = 1.0000084 USA volt$_{69}$. Accordingly, the total change in going from the old international volt (USA) to the modern absolute volt is: 1 international volt (USA) = 1.0003384 absolute USA volt$_{69}$. In 1948 the International Temperature Scale was revised [57] but differed from the 1927 scale only at temperatures above 630 °C and, therefore, out of the range of work done on standard cells by Wolff. However, in 1968 another revision of the International Temperature Scale was made [58] which did affect the precise value of the emf-temperature coefficient of standard cells; for example, $t_{68} - t_{48}$ is −0.004 °C at 10 °C, −0.007 °C at 20 °C, −0.009 °C at 30 °C and zero at the melting point of ice and the boiling point of water.

In view of the above changes in the basis of reference for the volt and in the International Temperature Scale, changes in the voltage standard and in the results obtained by Wolff on the emf-temperature coefficient become necessary. With these changes eq (29) and the alternate form, eq (31) become, respectively:

$$E = E_{20\,°C} - 0.000004064(t - 20)$$
$$- 0.00000095006(t - 20)^2 + 0.000000010034(t - 20)^3$$

$$(33)$$

and

$$E = E_{0\,°C} + 0.0000094019\,t$$
$$- 0.0000015521\,t^2 + 0.000000010034\,t^3 \qquad (34)$$

In table 3 the thermodynamic data for standard cells of the saturated cadmium sulfate type are given for temperatures from 0 to 43.6 °C [the transition temperature, $CdSO_4 \cdot \frac{8}{3} \, H_2O(s) = CdSO_4 \cdot H_2O(s)$], inclusive, as calculated from emf data and eq (33) or eq (34). In this table the changes in emf from international to absolute (1948), to absolute (1969), and for the different temperature scales are given. The thermodynamic data given herein are calculated from the most recent values of the emf, i.e., on V_{69} and t_{68}. The emf at 20 °C in

column 2 is that recommended by the International Committee on Electrical Units and Standards; it was based on the emf of cells prepared with mercurous sulfate made chemically or by dc electrolysis. Numerous investigations have indicated that mercurous sulfates prepared in different ways, providing they do not contain basic mercurous sulfate or mercuric ions, yield cells of the same emf. However, recent studies to be discussed in a subsequent paper, show that mercurous sulfate prepared by dc electrolysis gives cells with an emf exceeding those in column 5 of table 3 by 16.8 μV. This difference is small and amounts to only 3.24 J mol^{-1} (0.77 cal mol^{-1}) in ΔG and ΔH, see footnote to tables 3, 4, and 10.

The uncertainties listed, 1σ, are mean standard deviations obtained from the data on the 99 cells measured by Wolff, and includes an uncertainty of 5.4 μV[9] arising from the combined uncertainties in the absolute measurement of the ampere and the ohm.

5. Comparisons of Calorimetric and Equilibrium Data With Electrochemical (or Electrical) Data at 25 °C

Comparisons of calorimetric and equilibrium data with electrochemical data are given in table 4 for 25 °C. Insufficient data are available for direct comparisons at other temperatures. Six facts are evident from inspection of the data, namely:

(1) Remarkable agreement is obtained for ΔG, ΔH, and ΔS between the calorimetric and equilibrium data (sum 2) and electrochemical data in Part I if the emf data for cell (A) obtained by Hulett [34] and Getman [35] are used for reaction (e). This agreement may be coincidental in view of the uncertainties in the older heat data or results from a cancellation of errors, but even so it adds weight to the reliability of the postulated chemical reactions for standard cells of the saturated cadmium sulfate type. For example, Harned and Owen [62] state "It should be emphasized . . . that the nature of the chemical reactions, corresponding to a particular electrode, or cell, cannot be determined by electromotive force measurements alone. Cells reactions, no matter how simple and obvious, must be treated as hypothetical until it can be shown that thermodynamic quantities calculated from the electromotive force, $\Delta F[\Delta G]$, ΔH, equilibrium constants, etc. have been checked by other evidence."

(2) The difference of 1.722 J K^{-1} mol^{-1} (0.410 cal K^{-1} mol^{-1}) between the ΔC_p values (sum 2 and electrochemical) may well be accounted for by the data for cell (A) for which ΔC_p is zero. More careful measurements on cell (A) may well show that the emf of this cell as a function of temperature is second- or third-order rather than a linear function.

(3) The data show that the results of Parks and LaMer [39] for cell (A), although they give good agreement with calorimetric data for ΔG, yield

9 This is a root sum square value. Recently, John Clarke [59] gave the uncertainty as ±2.6 ppm (or μV); this is about one half the root sum square uncertainty in published values for the absolute ampere [60] and the absolute ohm [61].

TABLE 3. *Electromotive forces and thermodynamic data for standard cells of the saturated cadmium sulfate type*

Temperature		Electromotive force, V				Gibbs energy change, ΔG	
°C	Int	Abs$_{48}$ & t_{48}	Abs$_{69}$ & t_{48}	Abs$_{69}$ & t_{68}[b]	$\sigma_m(\mu V)$	(J mol⁻¹)[c]	(cal mol⁻¹)[d]
0.........	1.0186520	1.0189881	1.0189968	1.0189967	8.14	−196,639.9(4.8)	−46,998.0(1.1)
3.........	1.0186665	1.0190026	1.0190112	1.0190112	8.12	−196,642.7(4.8)	−46,998.6(1.1)
5.........	1.0186615	1.0189976	1.0190061	1.0190062	8.10	−196,641.7(4.8)	−46,998.4(1.1)
10.......	1.0186010	1.0189371	1.0189456	1.0189455	8.08.	−196,630.0(4.8)	−46,995.6(1.1)
15.......	1.0184780	1.0188141	1.0188226	1.0188224	8.07	−196,606.2(4.8)	−46,989.9(1.1)
18.......	1.0183773	1.0187133	1.0187219	1.0187216	8.06	−196,586.8(4.8)	−46,985.3(1.1)
20.......	1.0183000	1.0186360	1.0186445	1.0186442	8.06	−196,571.8(4.8)	−46,981.7(1.1)
25.......	1.0180745	1.0184105	1.0184190	1.0184185	8.07	−196,528.3(4.8)	−46,971.3(1.1)
28.......	1.0179195	1.0182554	1.0182639	1.0182634	8.08	−196,498.4(4.8)	−46,964.1(1.1)
30.......	1.0178090	1.0181448	1.0181533	1.0181528	8.08	−196,477.0(4.8)	−46,959.0(1.1)
35.......	1.0175110	1.0178467	1.0178552	1.0178547	8.09	−196,419.5(4.8)	−46,945.3(1.1)
40.......	1.0171880	1.0175236·	1.0175323	1.0175317	8.10	−196,357.2(4.8)	−46,930.4(1.1)
43.6 [a]...	1.0169446	1.0172797	1.0172886	1.0172878	8.11	−196,310.1(4.8)	−46,919.2(1.1)

	Emf-temperature coefficient, $\mu V\ K^{-1}$					Entropy change, ΔS		Enthalpy change, ΔH	
°C	Int	Abs$_{48}$ & t_{48}	Abs$_{69}$ & t_{48}	Abs$_{69}$ & t_{68}	$\sigma_m(\mu V)$	J K⁻¹ mol⁻¹	cal K⁻¹ mol⁻¹	(J mol⁻¹)[c]	(cal mol⁻¹)[d]
0.........	9.40	9.40	9.40	9.40	0.14	1.814(.027)	0.433(.006)	−196,147.4(11.8)	−46,880.3(2.8)
3.........	0.37	0.37	0.37	0.36	.11	0.069(.022)	.017(.005)	−196,624.8(10.4)	−46,994.5(2.5)
5.........	−5.35	−5.35	−5.36	−5.37	.10	−1.036(.020)	−0.248(.004)	−196,930.1(9.9)	−47,067.4(2.2)
10.......	−18.60	−18.61	−18.61	−18.63	.06	−3.595(.012)	−0.859(.003)	−197,647.1(7.7)	−47,238.8(2.0)
15.......	−30.35	−30.36	−30.36	−30.39	.04	−5.864(.008)	−1.402(.002)	−198,295.0(6.6)	−47,393.6(1.7)
18.......	−36.68	−36.70	−36.70	−36.72	.04	−7.086(.008)	−1.694(.001)	−198,649.3(6.6)	−47,478.2(1.3)
20.......	−40.60	−40.62	−40.61	−40.64	.04	−7.843(.008)	−1.874(.002)	−198,870.4(6.6)	−47,531.1(1.5)
25.......	−49.35	−49.37	−49.36	−49.39	.04	−9.531(.008)	−2.278(.002)	−199,370.3(6.6)	−47,650.5(1.6)
28.......	−53.88	−53.90	−53.89	−53.92	.04	−10.404(.008)	−2.487(.002)	−199,632.2(6.6)	−47,713.1(1.7)
30.......	−56.60	−56.62	−56.61	−56.63	.04	−10.929(.008)	−2.612(.002)	−199,790.7(6.7)	−47,750.8(1.7)
35.......	−62.35	−62.37	−62.35	−62.37	.06	−12.036(.012)	−2.877(.002)	−200,128.4(8.0)	−47,831.8(1.8)
40.......	−66.60	−66.62	−66.59	−66.60	.09	−12.853(.018)	−3.072(.004)	−200,380.6(10.0)	−47,692.1(2.3)
43.6 [a]...	−68.73	−68.76	−68.71	−68.72	.13	−13.261(.025)	−3.169(.007)	−200,506.4(12.3)	−47,927.0(3.3)

TABLE 3. *Electromotive etc.*—Continued

°C		Second derivative, d^2E/dT^2, μV K^{-1} K^{-1}					Heat-capacity change, ΔC_p	
	Int	Abs$_{48}$ & t_{48}	Abs$_{69}$ & t_{48}	Abs$_{69}$ & t_{68}	$\sigma_m(\mu$V)	J K^{-1} mol^{-1}	cal K^{-1} mol^{-1}
0.........	−3.100	−3.101	−3.102	−3.104	0.010	−163.62(.53)	−39.11(.13)
3.........	−2.920	−2.921	−2.921	−2.924	.008	−155.80(.43)	−37.24(.10)
5.........	−2.800	−2.801	−2.801	−2.803	.008	−150.46(.43)	−35.96(.10)
10	−2.500	−2.501	−2.501	−2.502	.006	−136.72(.33)	−32.68(.08)
15	−2.200	−2.201	−2.200	−2.201	.003	−122.40(.17)	−29.25(.04)
18	−2.020	−2.021	−2.020	−2.021	.001	−113.52(.06)	−27.13(.01)
20	−1.900	−1.901	−1.900	−1.900	.001	−107.49(.06)	−25.69(.01)
25	−1.600	−1.601	−1.599	−1.599	.001	−92.00(.06)	−21.99(.01)
28	−1.420	−1.420	−1.419	−1.418	.002	−82.43(.11)	−19.70(.02)
30	−1.300	−1.300	−1.299	−1.298	.003	−75.94(.18)	−18.14(.04)
35	−1.000	−1.000	−0.998	−0.997	.006	−59.29(.35)	−14.17(.09)
40	−0.700	−0.700	−0.698	−0.696	.008	−42.06(.48)	−10.05(.12)
43.6 [a]...	−0.484	−0.484	−0.481	−0.479	.009	−29.30(.55)	−7.00(.13)

[a] All values at 43.6 °C are extrapolated values.

[b] Based on combined results obtained with chemically-prepared and dc-electrolytic mercurous sulfate; the values are 18.6 μV higher for dc-electrolytic mercurous sulfate alone.

[c] Higher by 3.24 J mol^{-1} for dc-electrolytic mercurous sulfate alone.

[d] Higher by 0.77 cal mol^{-1} for dc-electrolytic mercurous sulfate alone.

results for ΔH, ΔS, and especially ΔC_p (actually of opposite sign) that differ widely from the electrochemical data on standard cells of the saturated cadmium sulfate type. Actually, Parks and LaMer gave too much weight to an apparent curvature in the variation of the emf of cell (A) with temperature.

(4) The enthalpy data of Papadopoulos and Giauque [21] lead to values for ΔG and ΔH that are lower than the electrochemical values by 301.3 J mol^{-1} (71.9 cal mol^{-1}) and 290.0 J mol^{-1} (69.3 cal mol^{-1}), respectively. These differences which amount, respectively, to only 0.16 percent and 0.15 percent, are beyond the uncertainties estimated by Papadopoulos and Giauque. Sometimes cadmium sulfate contains occluded sulfuric acid (especially if digested in sulfuric acid during the purification) which would cause a decrease in ΔG and ΔH for the cell reaction (see conclusions to this paper). Such occlusions could not

explain the above differences in ΔG and ΔH between the calorimetric and electromotive force data since the occlusions would have to amount to about 1 molal H_2SO_4 (see conclusions to this paper) which is entirely out of the range of possibility.

(5) If the alternate heat capacity data for reaction (a), discussed above, are used they yield a value for sum 2 which differs more from the electrochemical value than the value given in table 4 (actually, the alternate heat capacity data for reaction (a) yield −94.231 J K^{-1} mol^{-1} (−22.474 cal K^{-1} mol^{-1}) for sum 2 rather than the value shown).

(6) The enthalpy data of Papadoupolos and Giauque [21], if used with the enthalpy data of Bichowsky and Rossini [12], corrected to 25 °C, or the enthalpy data of Circular 500 [23] or the enthalpy data of revised NBS Circular [24, 30] still do not agree with the electrochemical data.

TABLE 4. *Comparison of calorimetric and equilibrium data with electromotive force data*

Part I − Based on table 1: experimental values of ΔG for reactions (b), (c), and (d) and of ΔH for reactions (a) and (b)

Calorimetric and equilibrium data	ΔG J mol^{-1}	ΔH J mol^{-1}	ΔS J K^{-1} mol^{-1}	ΔC_p J K^{-1} mol^{-1}
sum 2....................................	−196,558	−199,411	−9.576	[ϕ] −93.722
sum 3....................................	−196,563	−201,935	−18.026	110.538
Electrochemical data......................	[a] −196,528.3	[a] −199,370.0	−9.531	−92.00

Calorimetric and equilibrium data	cal mol^{-1}	cal mol^{-1}	cal K^{-1} mol^{-1}	cal K^{-1} mol^{-1}
sum 2....................................	−46,978.4	−47,660.2	−2.29	−22.400
sum 3....................................	−46,979.5	−48,263.6	−4.31	26.420
Electrochemical data......................	[b] −46,971.3	[b] −47,650.5	−2.278	−21.99

TABLE 4. *Comparison etc.*—Continued

Part II — Based on table 2: experimental values of ΔG for reaction (d) and of ΔH for reactions (a), (b), (c), and (d)

Calorimetric and equilibrium data	ΔG J mol^{-1}	ΔH J mol^{-1}	ΔS J K^{-1} mol^{-1}	ΔC_p J K^{-1} mol^{-1}
sum 2....................................	− 196,227	− 199,080	− 9.576	ϕ − 93.722
sum 3....................................	− 196,232	− 201,604	− 18.026	110.538
Electrochemical data......................	[a] − 196,528.3	[a] − 199,370.0	− 9.531	− 92.00

Calorimetric and equilibrium data	cal mol^{-1}	cal mol^{-1}	cal K^{-1} mol^{-1}	cal K^{-1} mol^{-1}
sum 2....................................	− 46,899.4	− 47,581.2	− 2.29	− 22.400
sum 3....................................	− 46,900.5	− 48,184.6	− 4.31	26.420
Electrochemical data......................	[b] − 46,971.3	[b] − 47,650.5	− 2.278	− 21.99

ϕ See tables 1 and 2 for a note on an alternate value.

[a] Higher by 3.24 J mol^{-1} for dc-electrolytic mercurous sulfate.

[b] Higher by 0.77 cal mol^{-1} for dc-electrolytic mercurous sulfate.

6. Range of Precision in Emf Results

In table 3 it is evident that the uncertainties in the data are greater at the two ends of the temperature range. For the emf, these reside in the experimental measurements but for the derived quantities, ΔH, ΔS, and ΔC_p, they may be dependent in addition on the emf-temperature function used to represent the data. Since the emf data available on the standard cell of the saturated cadmium sulfate type are known with high precision they may be used to illustrate the effect an emf-temperature function has on the derived thermodynamic data. Accordingly, the emf data of table 3 were fitted (method of least squares) to second-, third-, and fourth-order equations in the temperature of the form (fourth order shown):

$$E = E_{0\,°C} + \alpha t + \beta t^2 + \gamma t^3 + \delta t^4. \tag{35}$$

Also, since the literature [11, 62–65] is filled with results on the measurements of the emfs of galvanic cells to only 0.01 mV or 10 μV, and over a range of temperatures, the emf data of table 3 were rounded to 0.01 mV and then fitted (method of least squares) to second-, third-, and fourth-order equations in the temperature of the form of eq (35). The coefficients of the form equations for the several procedures are given in table 5.

Results are given in tables 6, 7, 8, and 9. In table 6 the emfs are given as obtained for fourth-, third-, and second-order equations and for emfs either known to 0.01 μV or rounded to 0.01 mV. Inspection shows that either third- or fourth-order equations may be used to represent the emfs.[10] Inspection also shows that the differences in ΔG are practically negligible between the fourth- and third-order fits. If the preci-

sion of the observations is lowered to 0.01 mV (table 7) the errors in ΔG are still practically negligible between the fourth- and third-order fits (see footnote 10). As expected, however, second-order equations are inadequate to represent E and ΔG with either resolutions of 0.1 μV or 0.01 mV in E.

For ΔS and ΔC_p the situation is quite different, see tables 8 and 9. Values of ΔS as given by fourth and third order equations are practically the same, except above 40 °C or at 0 °C for a resolution of 0.1μV in E but differ from 0.013 to 0.179 J K^{-1} mol^{-1} (0.007 to 0.043 cal K^{-1} mol^{-1}) for a resolution of 0.01 mV in E. Particular attention should be given to a comparison, say at 25 °C, between a fourth (or third) order fit to 0.1 μV in E and a *second* order fit to 0.01 mV in E (most common procedure reported in the literature); a difference of 0.607 (0.606) J K^{-1} mol^{-1} (0.145 cal K^{-1} mol^{-1}) is obtained. This difference is large and has mistakenly lead some observers [66–69], under similar cases, to conclude that the emf measurements

TABLE 5. *Coefficients in the equation:* $E = E_{0°} + \alpha t + \beta t^2 + \gamma t^3 + \delta t^4$

		(On V$_{69}$ and t_{68} scales)			
		(to 0.1 μV)			
Order	$E_{0°}$	$\alpha \times 10^6$	$\beta \times 10^6$	$\gamma \times 10^9$	$\delta \times 10^{11}$
4th	1.0189968	9.3415	− 1.5454	9.7894	0.27990
3d	1.0189967	9.4019	− 1.5521	10.034	....
2d	1.0190260	− 1.5507	− 0.89411	....	....
		(to 0.01 mV or 10 μV)			
4th	1.01900	9.9747	− 1.6498	13.828	− 4.2920
3d	1.01900	9.0481	− 1.5469	10.082	....
2d	1.01903	− 1.9569	− 0.88584	....	....

[10] Since the values in table 3 were generated from a third-order equation [see eqs (33) or (34)], the fit of a fourth-order equation would be no better than that of a third-order. However, derived quantities, especially ΔC_p, may be slightly different; actually the difference gives an estimate of the uncertainty in the derived quantity.

TABLE 6. *Results from fourth, third, and second order equations for the emf of standard cells of the saturated cadmium sulfate type as a function of temperature (to 0.1 μV)*

| Temperature, °C | Electromotive force, V | | | Δ in ΔG, | | | | Δ in ΔG, | |
| | | | | ΔE, μV | | J mol⁻¹ | | cal mol⁻¹ | |
	4th order	3d order	2d order	4–3	4–2	4–3	4–2	4–3	4–3
0...............	1.0189968	1.0189967	1.0190260	0.1	−29.2	0.02	−5.63	0.005	−1.35
3...............	1.0190112	1.0190112	1.0190133	0	−2.1	0	−0.41	0	−0.10
5...............	1.0190061	1.0190062	1.0189959	−0.1	10.2	−0.02	1.97	−0.005	0.47
10...............	1.0189455	1.0189455	1.0189211	0	24.4	0	4.71	0	1.13
15...............	1.0188224	1.0188224	1.0188012	0	21.2	0	4.09	0	0.98
18...............	1.0187217	1.0187216	1.0187084	0.1	13.3	0.02	2.57	0.005	0.61
20...............	1.0186443	1.0186442	1.0186373	0.1	7.0	.02	1.35	.005	.32
25...............	1.0184186	1.0184185	1.0184284	0.1	−9.8	.02	−1.89	.005	−0.45
28...............	1.0182635	1.0182634	1.0182816	0.1	−18.1	.02	−3.49	.005	−0.83
30...............	1.0181529	1.0181528	1.0181748	0.1	−21.9	.02	−4.23	.005	−1.01
35...............	1.0178547	1.0178547	1.0178764	0	−21.7	.02	−4.19	.005	−1.00
40...............	1.0175317	1.0175316	1.0175334	0.1	−1.7	.02	−0.33	.005	−0.08
43.6 [a]...............	1.0172880	1.0172878	1.0172587	0.2	29.3	.04	5.65	.01	1.35

[a] Extrapolated values.

TABLE 7. *Results from fourth, third, and second order equations for the emf of standard cells of the saturated cadmium sulfate type as a function of temperature (to 0.01 mV or 10 μV)*

| Temperature, °C | Electromotive force, V | | | Δ in ΔG, | | | | Δ in ΔG, | |
| | | | | ΔE, mV | | J mol⁻¹ | | cal mol⁻¹ | |
	4th order	3d order	2d order	4–3	4–2	4.3	4–2	4–3	4–2
0...............	1.01900	1.01900	1.01903	0	−0.03	0	−5.79	0	−1.38
3...............	1.01902	1.01901	1.01902	0.01	0	1.93	0	0.46	0
5...............	1.01901	1.01901	1.01900	0	0.01	0	1.93	0	0.46
10...............	1.01895	1.01895	1.01892	0	.03	0	5.79	0	1.38
15...............	1.01882	1.01882	1.01880	0	.02	0	3.86	0	0.92
18...............	1.01872	1.01872	1.01871	0	.01	0	1.93	0	.46
20...............	1.01864	1.01864	1.01864	0	0	0	0	0	0
25...............	1.01842	1.01842	1.01843	0	−0.01	0	−1.93	0	−0.46
28...............	1.01826	1.01826	1.01828	0	−0.02	0	−3.86	0	−0.92
30...............	1.01815	1.01815	1.01817	0	−0.02	0	−3.86	0	−0.92
35...............	1.01786	1.01785	1.01788	0.01	−0.02	1.93	−3.86	0.46	−0.92
40...............	1.01753	1.01753	1.01753	0	0	0	0	0	0
43.6 [a]...............	1.01729	1.01729	1.01726	0	0.03	0	5.79	0	1.38

[a] Extrapolated values.

are in error whereas, in fact, the differences arise from a lack of resolution or in imprecision of the instruments employed. For ΔC_p, this situation is even more marked, see table 9. Values of ΔC_p, as given by fourth and third order equations are nearly the same, although the fourth-order results are probably preferable, if the resolution in E is 0.1 μV. However, for a resolution of only 0.01 mV in E, large differences are found between fourth and third order fits, but the third-order fits agree more closely with the fourth and third order fits on 0.1 μV resolution in E; *third-order fits are, therefore, selected as final representations*, in line with eqs (29) and (31) given above. As above for ΔS, particular attention should be given to a comparison, say at 25 °C, between a third-order fit to 0.1 μV in E

and a *second* order fit to 0.01 mV in E (most common procedure reported in the literature); a difference of 9.93 J K⁻¹ mol⁻¹ (2.37 cal K⁻¹ mol⁻¹) is obtained. This value is again large and has mistakenly lead some observers [66–69], under similar cases, to conclude that the emf measurements are in error by as much as 1 mV whereas, in fact, the differences rest with the degree of resolution in the measuring equipment.

The situation in regard to both ΔS and ΔC_p is more serious at the extremes of temperature. This is shown in figures 1 and 2. It is obvious from these figures that ΔS and ΔC_p, as determined from emfs of different resolutions and equations of different order differ at the extremes of temperature and that in order to determine them, especially ΔC_p, at 0 °C and 40 °C

TABLE 8. *Entropy changes for reactions in standard cells of the saturated cadmium sulfate type as calculated by different functions*

| Temperature, °C | (to 0.1 µV in E) | | (to 0.01 mV or 10 µV in E) | | (to 0.1 µV in E) | | (to 0.01 mV or 10 µV in E) | | | | | |
| | J K⁻¹ mol⁻¹ | | | | | | cal K⁻¹ mol⁻¹ | | | | | |
	4th order	3d order	2d order	4th order	3d order	2d order	4th order	3d order	2d order	4th order	3d order	2d order
0	1.803	1.814	− 0.299	1.925	1.746	− 0.378	0.431	0.433	− 0.072	0.460	0.417	− 0.090
3	0.065	0.069	− 1.334	0.086	0.008	− 1.403	0.015	0.017	− 0.319	0.021	.002	− 0.335
5	− 1.037	− 1.036	− 2.025	− 1.063	− 1.093	− 2.087	− 0.248	− 0.248	− 0.484	− 0.254	− 0.261	− 0.499
10	− 3.592	− 3.595	− 3.750	− 3.675	− 3.640	− 3.797	− 0.859	− 0.859	− 0.896	− 0.878	− 0.870	− 0.907
15	− 5.861	− 5.864	− 5.475	− 5.937	− 5.896	− 5.506	− 1.401	− 1.402	− 1.309	− 1.419	− 1.409	− 1.316
18	− 7.084	− 7.086	− 6.511	− 7.136	− 7.109	− 6.532	− 1.693	− 1.694	− 1.556	− 1.706	− 1.699	− 1.561
20	− 7.841	− 7.843	− 7.201	− 7.873	− 7.860	− 7.215	− 1.874	− 1.874	− 1.721	− 1.882	− 1.879	− 1.725
25	− 9.532	− 9.531	− 8.926	− 9.508	− 9.532	− 8.925	− 2.278	− 2.278	− 2.133	− 2.272	− 2.278	− 2.133
28	− 10.406	− 10.404	− 9.961	− 10.355	− 10.395	− 9.950	− 2.487	− 2.487	− 2.381	− 2.475	− 2.484	− 2.378
30	− 10.931	− 10.929	− 10.652	− 10.867	− 10.912	− 10.634	− 2.612	− 2.612	− 2.546	− 2.597	− 2.608	− 2.542
35	− 12.036	− 12.036	− 12.377	− 11.975	− 12.000	− 12.344	− 2.877	− 2.877	− 2.958	− 2.862	− 2.868	− 2.950
40	− 12.849	− 12.853	− 14.102	− 12.856	− 12.796	− 14.053	− 3.071	− 3.072	− 3.371	− 3.073	− 3.058	− 3.359
43.6 [a]	− 13.248	− 13.261	− 15.345	− 13.365	− 13.189	− 15.284	− 3.166	− 3.169	− 3.667	− 3.194	− 3.152	− 3.653

[a] Extrapolated values.

TABLE 9. *Heat capacity changes for the reaction in standard cells of the saturated cadmium sulfate type as calculated by different functions*

| Temperature, °C | (to 0.1 µV in E) | | (to 0.01 mV or 10 µV in E) | | (to 0.1 µV in E) | | (to 0.01 mV or 10 µV in E) | | | | | |
| | J K⁻¹ mol⁻¹ | | | | | | cal K⁻¹ mol⁻¹ | | | | | |
	4th order	3d order	2d order	4th order	3d order	2d order	4th order	3d order	2d order	4th order	3d order	2d order
0	− 162.91	− 163.62	− 94.26	− 173.92	− 162.96	− 93.39	− 38.94	− 39.11	− 22.53	− 41.57	− 38.95	− 22.32
3	− 155.29	− 155.80	− 95.29	− 162.82	− 155.08	− 94.41	− 37.12	− 37.24	− 22.78	− 38.91	− 37.07	− 22.57
5	− 150.08	− 150.46	− 95.98	− 155.53	− 149.71	− 95.10	− 35.87	− 35.96	− 22.94	− 37.17	− 35.78	− 22.73
10	− 136.59	− 136.72	− 97.71	− 137.77	− 135.87	− 96.81	− 32.65	− 32.68	− 23.35	− 32.93	− 32.48	− 23.14
15	− 122.44	− 122.40	− 99.43	− 120.72	− 121.45	− 98.51	− 29.26	− 29.25	− 23.77	− 28.85	− 29.03	− 23.55
18	− 113.63	− 113.52	− 100.47	− 110.85	− 112.52	− 99.54	− 27.16	− 27.13	− 24.01	− 26.50	− 26.89	− 23.79
20	− 107.62	− 107.49	− 101.16	− 104.44	− 106.45	− 100.22	− 25.72	− 25.69	− 24.18	− 24.96	− 25.44	− 23.95
25	− 92.12	− 92.00	− 102.89	− 89.02	− 90.87	− 101.93	− 22.02	− 21.99	− 24.59	− 21.28	− 21.72	− 24.36
28	− 82.50	− 82.43	− 103.92	− 80.21	− 81.23	− 102.96	− 19.72	− 19.70	− 24.84	− 19.17	− 19.42	− 24.61
30	− 75.95	− 75.94	− 104.61	− 74.53	− 74.69	− 103.64	− 18.15	− 18.14	− 25.00	− 17.81	− 17.85	− 24.77
35	− 59.09	− 59.29	− 106.34	− 61.05	− 57.94	− 105.35	− 14.12	− 14.17	− 25.41	− 14.59	− 13.85	− 25.18
40	− 41.54	− 42.06	− 108.06	− 48.64	− 40.60	− 107.06	− 9.93	− 10.05	− 25.83	− 11.63	− 9.71	− 25.59
43.6 [a]	− 28.47	− 29.30	− 109.30	− 40.42	− 27.76	− 108.29	− 6.81	− 7.00	− 26.12	− 9.66	− 6.64	− 25.88

[a] Extrapolated values.
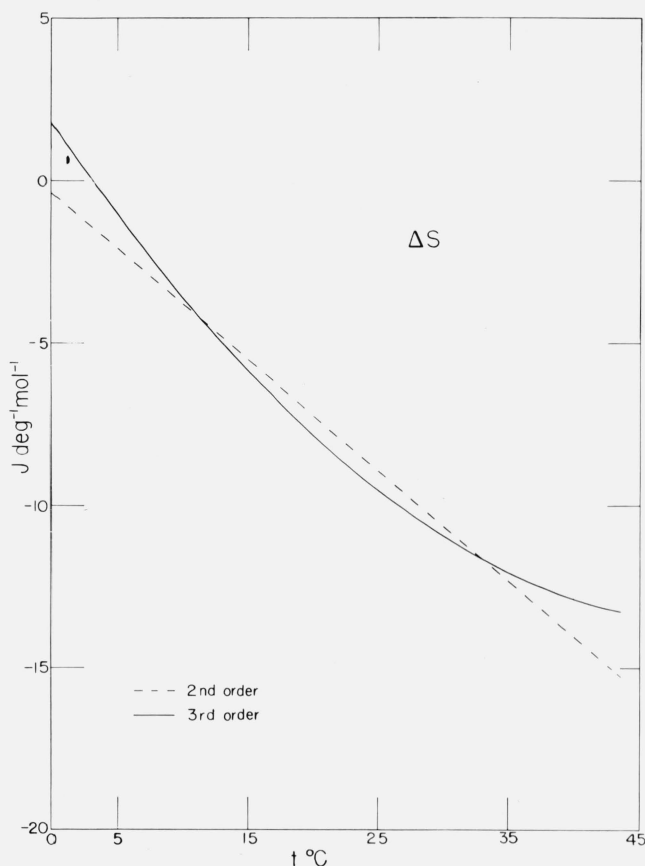
FIGURE 1. *Temperature variations in entropy change for the reaction in standard cells of the saturated cadmium sulfate type, as determined by different functions.*

(Fourth-order function gives nearly the same results as the third-order function and is, therefore, not shown)

with the certainty shown at 25 °C, higher resolution in emf and studies over a broader temperature range,[11] if possible, are necessary.

7. Alternate Emf Studies

In the foregoing sections calorimetric and equilibrium data relating to standard cells of the saturated cadmium sulfate type were compared with emf data of such cells. In this section emf data on various cells, which in combination, yield a saturated cadmium sulfate cell, will be compared with the emf of the saturated cadmium sulfate cell. Comparisons are limited to 25 °C where sufficient data are on hand.

Harned and Hamer [70] obtained 0.96495 V (converted to the V_{69} scale) at 25 °C for the emf of the cell:
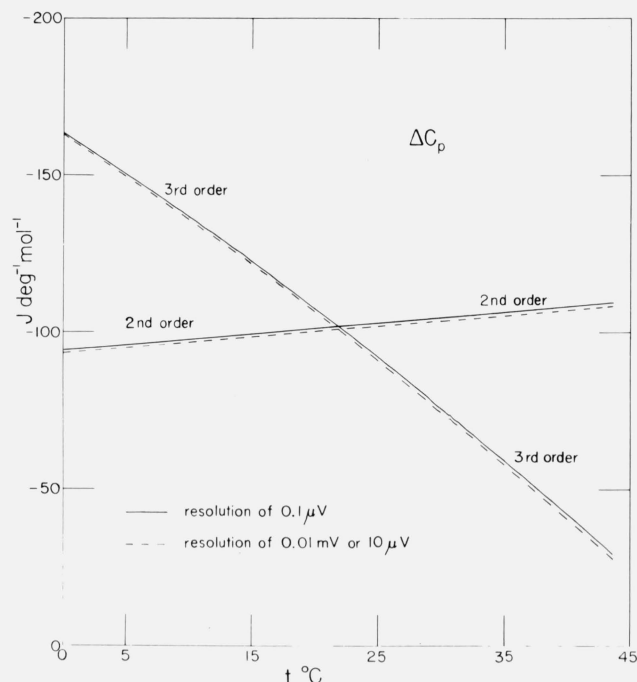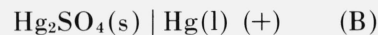

FIGURE 2. *Temperature variations in heat-capacity change for the reaction in standard cells of the saturated cadmium sulfate type, as determined by different functions.*

(Fourth-order function gives slightly different values than the third-order function, see text, table 9, for values).

$$(-)\ \text{Pb-Hg}(2p)\ |\ \text{PbSO}_4\,(s)|\text{Na}_2\,\text{SO}_4(\text{sol})|$$

$$\text{Hg}_2\text{SO}_4(s)\ |\ \text{Hg}(l)\ (+) \qquad (B)$$

LaMer and Parks [71] obtained 0.0013 V for the standard emf, E^0, of the cell:

$$(+)\ \text{Pb-Hg}(2p)\ |\ \text{PbSO}_4\,(s)\ |\ \text{CdSO}_4(a=1)\ |$$

$$\text{Cd-Hg}\ (11\%)\ (-) \qquad (C)$$
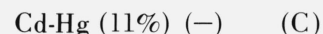
using the Gronwall, LaMer, and Sandved [72] treatment of interionic attraction to obtain E^0. Here a denotes activity of the solute. On converting to absolute volts and using recent values of the physical constants [1] and the dielectric constant of water [73], it was found that the Gronwall, LaMer, and Sandved treatment did not lead to constant values of E^0 for the emf data of LaMer and Parks at the various concentrations of $CdSO_4$. However, a straight-line extrapolation to $m=0$ to obtain E^0 follows by taking $CdSO_4$ as incompletely dissociated with a dissociation constant of 0.0059 mol kg^{-1} at 25 °C (an ion size of 3 Å was used in the extrapolation). Extrapolations to $m=0$ gives 0.00184 V instead of 0.0013 V, given by LaMer and Parks.[12]

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[11] It would appear, at first glance, that Vigoureux and Watts [54] met this criterion, since they carried their measurements to −20 °C thus making possible a good evaluation of ΔC_p at 0 °C. However, the emf goes through a maximum at 3 °C, thus limiting the effectiveness of a second-order equation to a narrow range of 3 °C to −20 °C, thereby not providing sufficient resolution for ΔC_p at 0 °C. In cases where a maximum or minimum in emf did not occur extension of measurements to −20 °C or lower would enhance the evaluation of ΔC_p by a second-order equation. However, higher order equations should be used.

[12] In their 1931 paper LaMer and Parks gave results at 0 and 25 °C. In their 1933 paper (stated to give better results) they gave results of measurments at 0, 10, 20, and 30 °C, but not for 25 °C. Using the above treatment, i.e., taking $CdSO_4$ as incompletely dissociated, E^0 was calculated at these four temperatures which were then fitted to a third-order equation using least squares to give: E^0 (in volts) $= 0.01698 - 0.0003588\ t - 0.000012949\ t^2 + 0.00000012328\ t^3$. At 25 °C this equation yields 0.00184 V, the value given above for E^0; also interpolation of the data for the dissociation constants for these temperatures gives 0.0059 mol kg^{-1} for the dissociation constant for 25 °C.

Combining cells (B) and (C) gives 0.96679 V for the cell:

$$(-) \text{ Cd-Hg}(11\%) \mid \text{CdSO}_4(a=1) \mid \text{Hg}_2\text{SO}_4(\text{s}) \mid$$

$$\text{Hg}(\text{l}) \ (+) \qquad (D)$$
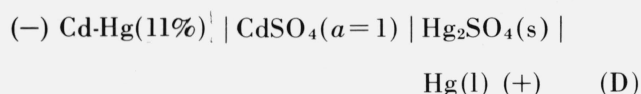
which is the cadmium sulfate standard cell but for a CdSO_4 solution having an activity of one rather than for a saturated solution of CdSO_4. This emf may be converted to that for a saturated solution of CdSO_4 using the Nernst equation:

$$E_{\text{standard cell}} = E^0_{\text{standard cell}} - \frac{RT}{F} \ln m_{\text{CdSO}_4} \gamma_{\text{CdSO}_4} \quad (36)$$

where

$E^0_{\text{standard cell}} = 0.96679$ V, given above, m is the molality of a saturated solution of CdSO_4, 3.6789 [6], γ is the mean stoichiometric activity coefficient of CdSO_4, and R, T, and F have the significance given previously in this paper. Harned and Owen [74] and Robinson and Stokes [75] list values of γ from 0.1 to 3.5 molal. Fitting averages of their values above 2 m (γ goes through a minimum at 2.5 m) to an equation of the form:
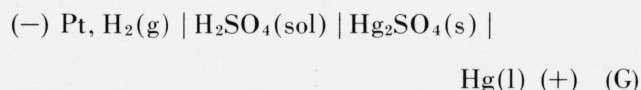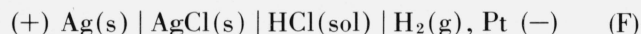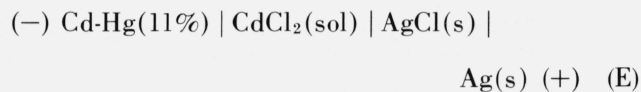
$$\log \gamma = \frac{-4A\sqrt{I}}{1 + 1.5\sqrt{I}} + aI + bI^2 + cI^3 \quad (37)$$

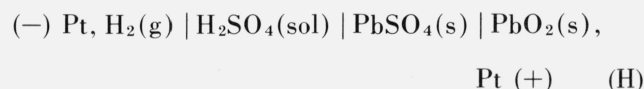where $A = 0.5108$ [76] and I = ionic strength, gives:

$$\log \gamma = \frac{-2.0432\sqrt{I}}{1 + 1.5\sqrt{I}} - 0.10780 I$$

$$+ 0.0091117 I^2 - 0.00020852 I^3 \quad (38)$$

where coefficients a, b, and c were obtained by the method of least squares. This equation yields 0.03646 for γ for a saturated solution of CdSO_4 at 25 °C. Substituting this value in eq (36) together with the above values for m and E^0 leads to 1.01840 V for a "neutral" standard cell of the saturated cadmium sulfate type at 25 °C which agrees remarkably well with the observed value, 1.0184185 V, see table 3. This agreement is remarkable since the emfs used in obtaining E^0 were measured to only 0.01 mV.

Another approach to the emf of the standard cell of the saturated cadmium sulfate type may be made using a combination of the three cells:

$$(-) \text{ Cd-Hg}(11\%) \mid \text{CdCl}_2(\text{sol}) \mid \text{AgCl}(\text{s}) \mid$$

$$\text{Ag}(\text{s}) \ (+) \qquad (E)$$

$$(+) \text{ Ag}(\text{s}) \mid \text{AgCl}(\text{s}) \mid \text{HCl}(\text{sol}) \mid \text{H}_2(\text{g}), \text{Pt} \ (-) \qquad (F)$$

$$(-) \text{ Pt}, \text{H}_2(\text{g}) \mid \text{H}_2\text{SO}_4(\text{sol}) \mid \text{Hg}_2\text{SO}_4(\text{s}) \mid$$

$$\text{Hg}(\text{l}) \ (+) \qquad (G)$$

where g = gas and the other symbols have the significance given above. The emfs of these cells were measured for a series of concentrations and temperatures by Harned and Fitzgerald [77], Harned and Ehlers [78], and Harned and Hamer [79], respectively. For the first two cells, the authors obtained the standard potential, E^0, of the cells directly by standard extrapolations using the Debye-Hückel [80] theory of interionic attraction. For the third cell, however, owing to the very high solubility of Hg_2SO_4 in dilute solutions of sulfuric acid, the authors calculated E^0 using values of the activity coefficients of H_2SO_4 obtained from emf measurements of the cell [81]:

$$(-) \text{ Pt}, \text{H}_2(\text{g}) \mid \text{H}_2\text{SO}_4(\text{sol}) \mid \text{PbSO}_4(\text{s}) \mid \text{PbO}_2(\text{s}),$$

$$\text{Pt} \ (+) \qquad (H)$$

The authors measured the emfs of cells (E), (F), (G), and (H) in international volts and for extrapolations to $m = 0$ to obtain E^0, used the values of the physical constants then in use [82]; their results were converted here to absolute volts using the factor given above, and the presently recommended values for the physical constants [1] were used in the extrapolations to $m = 0$ to obtain values of E^0. For 25 °C, the E^0 values of cells (E), (F), and (G) thus obtained are 0.57399 V,[13] 0.22247 V, and 0.61536 V, respectively. These lead to 0.96688 V for cell (D) whereas the first method using cells (B) and (C) leads to 0.96679 V; this is not a bad agreement considering that the second method involves three different cells, one of which contains an incompletely dissociated electrolyte, CdCl_2, and another involves indirect calculations using a combination of results on two cells, cells (G) and (H). This latter value gives 1.01849 V for the emf of the standard cell of the saturated cadmium sulfate type at 25 °C. The agreement here with the observed emf is not as good as in the first case, but is still within the probable error of the measurements; more is given later on this agreement.

The emfs of cells (E), (F), (G), and (H) have been measured by others. Horsch [84], Lucasse [85], Quintin [86], and Treumann and Ferris [87] measured the emfs of cell (E) at a series of concentrations, except that Horsch used a 4.6-percent amalgam and Lucasse, one of unstated percentage. When Horsch's emfs are corrected from 4.6 percent to 11 percent amalgam by adding 0.00293 V, derivable from Smith's [36] measurements, his results agree closely on the average with the results of Harned and Fitzgerald, except below 0.00025 molal where Horsch stated that his results deviated from a smooth curve. Lucasse's amalgams

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[13] Harned and Fitzgerald [77] gave 0.57390 international volt for E^0 (a typographical error listed this as 0.57300 international volt) based on a dissociation constant of 0.011 mol kg^{-1} for the equilibrium: $\text{CdCl}^+ \rightleftharpoons \text{Cd}^{++} + \text{Cl}^-$ and 5 Å for the ion-size parameter in treating interionic attraction; they assumed that the dissociation: $\text{CdCl}_2 \rightarrow \text{CdCl}^+ + \text{Cl}^-$ was complete. Their E^0 value becomes 0.57409 absolute volts using the factor between international and absolute volts given above. They stated their experimental accuracy to be of the order of 0.1 mV. Using more recent values for the physical constants [1] and T [1] and the dielectric constant of water [73] it was found that a better fit to their data was obtained using 0.010 mol kg^{-1} for the dissociation constant and 7 Å for the ion-size parameter; these lead to 0.57399 absolute volt for E^0. Incidentally, Reghellato and Davies [83] obtained 0.0101 mol l^{-1} for the dissociation constant from electrolytic conductivity measurements.

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apparently were 1½ percent in cadmium since, if the difference in the potentials between 1½- and 11-percent amalgams is added to Lucasse's emfs they then agree excellently with those of Harned and Fitzgerald at all concentrations above 0.01 m; however, Lucasse's measurements were not made to sufficiently low concentrations to afford an evaluation of E^0. Quintin's emfs agree closely with those of Harned and Fitzgerald; her emfs yield 0.57395 V for E^0 for cell (E), or 0.04 mV lower than the value obtained from the measurements of Harned and Fitzgerald. Quintin's value for E^0 gives 0.96683 V for cell (D) which yields with the E^0 values for cells (F) and (G) a value of 1.01844 V for the standard cell of the saturated cadmium sulfate type. This value agrees better with the observed emf of a standard cell than the data of Harned and Fitzgerald. However, the standard deviation of the mean of Quintin's measurements is 0.12_8 mV as compared with 0.03_4 mV for Harned and Fitzgerald's results.

The emf of cell (F) has been measured by others in addition to the one cited above. For E^0 at 25 °C Prentiss and Scatchard [88] arrived at a value of 0.22250 V from the earlier measurements excluding those of Harned and Ehlers [78]. MacInnes [89] gave 0.22258 V, Hamer [90] 0.22239 V, Harned and Paxton [91] 0.22239 V, and Bates and Bower [92] 0.22234 V; where necessary these were converted to absolute volts using the factor between international and absolute volts given above. The differences in these values are generally attributed to the differences in the methods of preparation of the silver-silver chloride electrodes or methods of extrapolation to $m = 0$ [88]. The average of these values, namely, 0.22244 V agrees within 0.03 mV of the value of Harned and Ehlers, used above. Since Harned and Fitzgerald for cell (E) and Harned and Ehlers for cell (F) used silver-silver chloride electrodes prepared in the same way, the characteristics of the silver-silver chloride electrode should be eliminated if we use their E^0 values in arriving at E^0 for cell (D) since we take the difference of cells (E) and (F) in arriving at E^0 for cell (D).

The emfs of cell (G) have been measured by many in addition to those cited above [79]. Results are listed in table 10. Those marked with a superscript b were calculated here; the authors did not give values for E^0. The value of Harned and Hamer when combined with the E^0 value for the cadmium-amalgam electrode and the m and γ of saturated $CdSO_4$ yields an emf for the standard cell of the saturated cadmium sulfate type that agrees well with the observed emf. The average of the values of Harned and Sturges [98], Randall and Stone [101], Trimble and Ebert [102], Müller and Reuther [104], and Beck et al., namely, 0.61555 V (or 0.61551 V, see footnote e of table 10) agrees within 0.19 (or 0.15) mV of the value of Harned and Hamer.

The recent values for E^0 for cell (G) of Beck, Dobson, and Wynne-Jones [105] and of Covington, Dobson, and Wynne-Jones [69] are not in good agreement, differing by 0.31 mV; the first [105] agrees fairly closely with earlier value of Harned and Hamer [79] whereas the latter [69] agrees fairly well with the very early value of Lewis and Lacey [95]. However, when combined with the E^0 value of the cadmium-amalgam electrode and

TABLE 10. *Values of the standard potential of the mercury-mercurous sulfate electrode and of the standard cell* ($a = 1$) *and the corresponding electromotive force of the saturated standard cell at 25 °C*

(all values on V_{69} scale)				
Date	Experimenters	Hg, Hg_2SO_4 E^0	Standard cell	
			E^0	E(sat.)
		Volt	*Volt*	*Volts*
1910	Brønsted [93]	a,b 0.6170	0.96843	1.02004
1914	Lewis and Lacey [95]	.6129	.96433	1.01594
1918	Randall and Cushman [94]	c.6215	.97293	1.02454
1921	Ferguson and France [97]	b.6199	.97133	1.02294
1925	Harned and Sturges [98]	b.61534	.96677	1.01838
1926	Åkerlöf [99]	b.6168	.96823	1.01984
1927	Randall and Langford [100]	d.6245	.97593	1.02754
1929	Randall and Stone [101]	b.61550	.96693	1.01854
1933	Trimble and Ebert [102]	b.6156	.96703	1.01864
1933	MacDougall and Blumer [103]	.6294	.98083	1.03244
1935	Harned and Hamer [79]	.61536	.96679	1.01840
1942	Müller and Reuther [104]	.6155	.96693	1.01854
1960	Beck, Dobson, and Wynne-Jones [105]	e.61582	.96725	1.01886
1965	Covington, Dobson, and Wynne-Jones [69]	.61251	.96394	1.01555
1969	Gardiner, Mitchell, and Cobble [67]	f.61251	.96394	1.01555
1970	Sharma and Prasad [107]	.6135	.96493	1.01564

Observed emf of standard cell g = 1.0184186

a See Randall and Cushman [94]; these authors reported necessary corrections for Brønsted's data and reported some earlier results of Arthur Edgar who, however, measured his emfs only to 1 mV.
b Calculated here from emfs for 0.05 to 0.21 m using activity coefficients of sulfuric acid given in reference [79].
c Given in Lewis and Randall [96].
d Stated to be a provisional value.
e Ives and Smith [106] listed this value as 0.61560 V−becomes 0.61561 V on V_{69} scale; reason for discrepancy is unknown.
f Selected by these authors in a recalculation of the activity coefficients of sulfuric acid, i.e., the 1965 value.
g For dc-electrolytic mercurous sulfate exclusively 1.0184354 V.

the m and γ of saturated cadmium sulfate, the E^0 value of Covington et al. for the mercury-mercurous sulfate electrode yields a value for the emf of the standard cell of the saturated cadmium sulfate type which is at great variance (-3.3 mV) from the observed value. There can be little doubt that their E^0 value for the mercury-mercurous sulfate electrode is in error. The value of Beck et al. for E^0 of the mercury-mercurous sulfate electrode leads to a better value for the emf of the standard cell of the saturated cadmium sulfate type than does that of Covington et al., but even so yields a value that is about 0.45 mV above the observed value.

These additional E^0 values for cells (E), (F), and (G) show that the original selection of data [77−79] for these three cells is justified. The slight difference of 0.09 mV in the calculated value of the emf of the

standard cell of the saturated cadmium sulfate type as given by cells (B) and (C) on the one hand and by cells (E), (F), and (G) on the other hand can be attributed largely to uncertainties in extrapolations to obtain E^0 values, especially for cell (E) wherein cadmium chloride may show more complex dissociation [108] than assumed by Harned and Fitzgerald. The total uncertainty of 0.09 mV is, therefore, attributed entirely to cell (E), which is within the uncertainty stated by the authors.

The E^0 for the positive electrode of the standard cell is obtained directly from cell (G),[14] while the E^0 for the negative electrode of the standard cell is obtained from the E^0's of cells (B), (C), and (G), or $E_B + E_C - E_G$. These give:

	E^0, V
Positive electrode	0.61536
Negative electrode	−0.35143
Complete cell	0.96679

which give for a saturated solution of cadmium sulfate (assuming that $\gamma_{Cd^{++}} = \gamma_{SO_4} = \gamma_{CdSO_4}$):

	E, V	
Positive electrode	0.64117	0.6411743
Negative electrode	−0.37724	−0.3772443
Complete cell	1.01841	1.0184186
Observed value		1.0184186

As a basis for measurement, the difference of 8.6 μV between the calculated and observed value for the complete cell may be divided between the values for the two electrodes to give the values in the last column.

8. Reproducibility

The good check between calorimetric and equilibrium data and emf data of standard cells of the saturated cadmium sulfate type on the one hand and between emf data on galvanic cells related to the standard cell and the emf of the standard cell itself on the other hand, given above, does not imply that standard cells having the emfs given above to 0.1 μV (see table 3), can be made easily and readily without great care. Cells can be made, however, without extreme care that will agree in emf to 0.01 mV as illustrated by data in table 3.

Various reasons have been advanced why standard cells cannot be made that agree in emf to 0.1 μV. The main reasons are: (1) differences in acidity of the solution, (2) differences in acidity between the two distinct electrodes of the cell, (3) differences in extent of reactions between the solution and the cell container (glass), (4) differences in the size of crystals of both cadmium and mercurous sulfates, (5) undersaturation or oversaturation with cadmium sulfate at either one or both of the electrodes, (6) undersaturation of the solution with mercurous sulfate at the positive electrode,

(7) presence of mercuric ions at the positive electrode, (8) amalgam composition, (9) impurities, and (10) cell construction. Of these the ones relating to acidity are the most important; amalgam composition, saturation of the solution with cadmium sulfate at both electrodes and with mercurous sulfate at the positive electrode, crystal size, and amount of mercuric ions can be readily controlled. Also by purification, impurities can be reduced to a minimum; impurities with higher electrical potential than hydrogen must be eliminated. Soluble trace impurities, although they may have no effect on the stability of the cell, may alter the initial emf slightly through a solvent effect affecting the value of the activity coefficient of cadmium sulfate. Thermodynamically, the emf and emf-temperature coefficient are independent of cell construction; however, the rate of attainment of equilibrium after a temperature change can be affected by cell design. The H-form of cell used here and in modern cells permits attainment of temperature equilibrium in relatively short times.

The acidity of the solution and the distribution of the acid throughout the cell affect the emf. Increases in acidity in the cell as a whole decrease the emf of the cell [5, 50, 55, 109, 110]. Increase in acidity at the negative electrode alone increases the emf of the cell while more acid at the positive electrode alone decreases the emf of the cell [36]; these arise from changes in the potential of the acidified electrode and a liquid-junction potential at the interface of the neutral and acid compartments of the cell. If the acid is confined to the region of the mercury-mercurous sulfate paste the liquid-junction potential will differ from that produced if the acid extends to a region above the paste.

Low concentrations of H_2SO_4 (less than 0.1 N) affect only slightly the emf-temperature coefficient of the cell [4, 49, 54, 55]. The relation between the emf-temperature coefficient and the acidity appears to be irregular; more on this will be given in a subsequent paper. Addition of sulfuric acid, through a common-ion effect, decreases the solubility of cadmium sulfate but the total sulfate concentration ($SO_4^=$ ion from $CdSO_4 +$ $SO_4^=$ ion from H_2SO_4) exceeds that of $CdSO_4$ alone. However, the activity coefficient of $CdSO_4$ is decreased by the addition of H_2SO_4, so that the activity of $CdSO_4$ in water or in water-sulfuric acid mixtures is nearly constant. High concentrations of H_2SO_4, of the order of 1 N (or 0.5 M) increase the emf-temperature coefficient of the cell [49, 50]. However, concentrations of H_2SO_4 this high cause excessive gassing at the cadmium-amalgam electrode and are not used for precision cells.

Even though acid affects the initial emf of standard cells, the long-range stability of the cells is affected only slightly. This is evident from the long-range stability exhibited by standard cells of different acidity maintained at the National Bureau of Standards [5, 111] and from international comparisons of cells of various acidities [112]. In the ultimate, stability in emf is the important criterion in the maintenance of the unit of emf, rather than the actual value of the emf. Thermodynamically, however, the value of the emf is all important, in that it gives a measure of the Gibbs energy change or maximum available energy of the cell, and an

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[14] As stated earlier, data from cell (H) are required to get E^0 for cell (G).

insight into whether the assigned value is consistent with related thermodynamic quantities.

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9. References

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