Summary

Tin added to a dilute, aqueous, hot, 1% solution of $CuSO_4:5H_2O$ containing less than 12 cc. of concentrated sulfuric acid per liter precipitates an alloy corresponding in composition and crystal structure to that of the Cu_3Sn phase prepared by fusion. When the solution contains more than 20 cc. of concentrated sulfuric acid per liter, an alloy corresponding in composition and crystal structure to that of the α-phase of the copper–tin system is precipitated.

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The Heat of Dilution and the Partial Molal Heat Capacity of Zinc Sulfate from the Electromotive Force of Galvanic Cells

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I. Introduction

Although the use of the Gibbs–Helmholtz equation has been recognized for many years as a reliable procedure for calculating changes in heat content in chemical processes from the e. m. f. measurements of galvanic cells, the applications have been restricted almost exclusively to processes involving displacement reactions between metals and their salts.

In spite of the renewed interest in the theoretical interpretation of the caloric properties of electrolytes in the region of high dilution, little use has been made of the method for the determination of heats of dilution of electrolytes in this important region.[2]

The paucity of galvanic cells which will yield reversible e. m. f.'s at the low concentrations necessary for an unambiguous extrapolation to infinite dilution is undoubtedly one reason for the neglect of the method. Skepticism of the reliability of methods involving differentiation for their numerical solution is another. The latter objection, however, is not peculiar to the e. m. f. method, for in the calorimetric method it is necessary to differentiate the measured integral heat of dilution in respect to concentration to calculate the partial molal quantity which is obtained in the e. m. f. method by differentiating the e. m. f. values with respect to temperature.

[1] This is a second paper constructed from a dissertation submitted in December, 1930, by Irving A. Cowperthwaite to the Faculty of Pure Science of Columbia University in partial fulfilment of the requirements for the degree of Doctor of Philosophy. This paper was presented at the Buffalo (1931) meeting of the Society. The first paper appeared in THIS JOURNAL, **53**, 4333 (1931).

[2] Recently Harned and Nims [THIS JOURNAL, **54**, 423 (1932)] have computed the partial molal heat of dilution and partial molal heat capacity of sodium chloride solution from 0.05 *m* to 4 *m* against the reference state of the 0.1 *m* solution from e. m. f. measurements through the temperature range of 0–40°. See also Harned and Murphy, *ibid.*, **53**, 8 (1931); Lewis and Randall, "Thermodynamics and the Free Energy of Chemical Substances," McGraw-Hill Book Co., Inc., New York, 1923, p. 392; Ellis, THIS JOURNAL, **38**, 737 (1916).

In the previous paper[3] it was shown that the e. m. f. of the cell

$$\text{Zn-Hg (two phase)} \mid ZnSO_4\,(m),\ PbSO_4\,(s) \mid \text{Pb-Hg (two phase)} \tag{1}$$

corresponding to the process

$$Zn\,(s) + PbSO_4\,(s) = ZnSO_4\,(m) + Pb\,(s) \tag{2}$$

could be measured with a precision of ±0.05 mv. to concentrations as low as 0.0005 *m* at temperatures of 0, 12.5, 25, 37.5 and 50°. This cell is consequently well suited for our purpose.

The essential improvement which we offer in the use of this method of computing heat quantities consists in the application of the theoretical equations of Gronwall, La Mer and Sandved[4] as a more legitimate means of extrapolating the e. m. f. data to infinite dilution for an exact evaluation of E° as compared to the customary graphical methods. The accurate values of E° thus obtained permit the computation of $\overline{L}_2$ (the relative partial molal heat content) and $\bar{c}_p - \bar{c}_p^\circ$ (the relative partial molal heat capacity) for the solute. The reference state for each of these properties is infinite dilution. The variation of these properties with concentration is the result of interionic attraction.

Inasmuch as the subsequent differentiation process for determining the temperature coefficients of the e. m. f. will exaggerate any experimental error in the individual measurements, we have eliminated these variations as far as possible by employing smoothed values of $E^{\circ\prime}$ (see Eq. 3) computed on the basis of the theoretical equations using the best values of E° and the parameter "*a*" as determined from the original data.[3] This procedure does not eliminate the experimental error in any given measurement, but distributes it more equitably over the entire concentration range rather than focusing it upon one particular concentration. Consequently this method is superior to the customary graphical smoothing since all the experimental data are involved uniformly in the smoothing process.

TABLE I

SMOOTHED VALUES OF $E^{\circ\prime}$

m	0°	12.5°	25°	37.5°	50°
0	0.43594	0.42407	0.41086	0.39628	0.38192
.0005	.44149	.43001	.41724	.40320	.38924
.001	.44386	.43256	.41999	.40620	.39238
.002	.44704	.43596	.42365	.41018	.39653
.005	.45247	.44176	.42984	.41690	.40349
.01	.45731	.44690	.43531	.42276	.40953

II. Theoretical

In Table I

$$E^{\circ\prime} = E + \frac{\nu}{n}\frac{RT}{F}\ln m \tag{3}$$

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(3) Cowperthwaite and La Mer, THIS JOURNAL, **53**, 4333 (1931).

(4) Gronwall, La Mer and Sandved, *Physik. Z.*, **29**, 358 (1928).

where E is the measured e. m. f. at the molality m. From the expression

$$E = E^\circ - \frac{\nu}{n}\frac{RT}{F}\ln m - \frac{\nu}{n}\frac{RT}{F}\ln f \qquad (4)$$

where f is the activity coefficient of the salt at molality m, and E° is a constant

$$E^{\circ\prime} = E^\circ - \frac{\nu}{n}\frac{RT}{F}\ln f\text{[5]} \qquad (5)$$

Substituting for E its equivalent $E^{\circ\prime} - \nu\, RT/nF \ln m$ as defined in equation (3) in the Gibbs–Helmholtz equation

$$-\Delta H = nF\left(E - T\frac{\partial E}{\partial T}\right) \qquad (6)$$

and collecting terms

$$-\Delta H = nF\left(E^{\circ\prime} - T\frac{\partial E^{\circ\prime}}{\partial T}\right) \qquad (7)$$

Equation (7) is amenable to numerical treatment since $E^{\circ\prime}$ extrapolates to a finite value (E°) whereas E in equation (6) becomes infinite when $m = 0$.

Substituting numerical values for $E^{\circ\prime}$ and $dE^{\circ\prime}/dt$ determined for a given molality m and temperature T in equation (7) yields $-\Delta H$ the decrease in heat content corresponding to the cell process

$$\text{Zn(solid, saturated with Hg)} + \text{PbSO}_4\text{(s)} = \text{ZnSO}_4\text{(m)} + \text{Pb(solid, saturated with Hg)} \qquad (8)$$

Whereas substitution of the values of E° [$= E^{\circ\prime}$ $(m = 0)$] and dE°/dt yield $-\Delta H(m = 0)$, the corresponding thermal quantity for the process (9) when the molality of zinc sulfate is zero.

$$\text{Zn(solid, saturated with Hg)} + \text{PbSO}_4\text{(s)} = \text{ZnSO}_4(\text{m} = 0) + \text{Pb(solid, saturated with Hg)} \qquad (9)$$

If we subtract equation (8) from equation (9), the solids cancel and the heat effect $\bar{L}_2$ corresponding to the transfer of one mole of zinc sulfate from molality (m) to infinite dilution remains

$$\text{ZnSO}_4(m) = \text{ZnSO}_4(m = 0) \qquad (10)$$

$\bar{L}_2$, the relative partial molal heat content of aqueous zinc sulfate is defined by

$$-\Delta H\,(\text{Equation 10}) = \bar{H}_2 - \bar{H}^\circ_2 = \bar{L}_2 \qquad (11)$$

By subtracting the Gibbs–Helmholtz equation corresponding to process (8) from that corresponding to process (9)

$$\bar{L}_2 = nF\left[(E^\circ - E^{\circ\prime}) - T\left(\frac{\partial(E^\circ - E^{\circ\prime})}{\partial T}\right)\right] \qquad (12)$$

Substituting the value of $E^\circ - E^{\circ\prime}$ from equation (5)

$$\bar{L}_2 = nF\left[\frac{\nu}{n}\frac{RT}{F}\ln f - T\left(\frac{\partial\left(\frac{\nu}{n}\frac{RT}{F}\ln f\right)}{\partial T}\right)\right] \qquad (13)$$

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(5) In the special case of a bi-bivalent electrolyte, like zinc sulfate to which this paper is restricted, $\nu = 2$ (the number of ions per mole of salt) and $n = 2$ (the number of Faradays involved in the cell process) so that the factor ν/n equals unity. The symbol f will always refer to $f_\pm$ the geometric mean activity coefficient of the salt, and similarly $m = m_\pm$.

Performing the indicated differentiation and collecting terms, the expression[6] for $\bar{L}_2$ can be written.

$$\bar{L}_2 = -\nu RT^2 \frac{\partial \ln f}{\partial T} \tag{14}$$

The limiting law for $\bar{L}_2$ follows by substituting in (14) the expression for $\ln f$ given by the limiting form of the Debye–Hückel theory[7]

$$\bar{L}_2 = \nu RT^2 \frac{\partial}{\partial T}\left(\frac{\epsilon^2 z^2}{kTDa}\cdot\frac{1}{2}\cdot x\right) \tag{15}$$

On carrying out the indicated differentiation, the following expression results[8]

$$\bar{L}_2 = -\frac{3}{4}\nu \frac{R\epsilon^2 z^2}{kD}\kappa\left(1 + \frac{T}{D}\frac{dD}{dT} + \frac{1}{3}\frac{T}{V}\frac{dV}{dT}\right) \tag{16}$$

For a bi-bivalent electrolyte where $\nu = 2$

$$\bar{L}_2 = 5735\ \sqrt{c} \text{ at } 25^\circ \text{ for } c \longrightarrow 0 \tag{17}$$

$$\bar{L}_2 = 4620\ \sqrt{c} \text{ at } 12.5^\circ \text{ for } c \longrightarrow 0 \tag{18}$$

Substituting equation (7) in Kirchhoff's formula

$$\Delta C_p = \frac{\partial \Delta H}{\partial T} \tag{19}$$

and simplifying

$$\Delta C_p = nFT\left(\frac{\partial^2 E^{\circ\prime}}{\partial T^2}\right) \tag{20}$$

By subtracting the change in heat capacity for the cell process at infinite dilution from that at molality m, we obtain the change in partial molal heat capacity of the zinc sulfate between molality m and $m = 0$. By means of the same type of transformations used in deriving (12) and (14)

$$\bar{C}_p - \bar{C}_p^\circ = nFT\frac{\partial^2}{\partial T^2}(E^{\circ\prime} - E^\circ) \tag{21}$$

$$\bar{C}_p - \bar{C}_p^\circ = -\frac{\partial}{\partial T}\left[\nu RT^2 \frac{\partial}{\partial T}(\ln f)\right] \tag{22}$$

By introducing the Debye–Hückel limiting law for $\ln f$ and performing the differentiations, we get equation (23)

$$\bar{C}_p - \bar{C}_p^\circ = -\frac{3}{8}\frac{\nu R\epsilon^2 z^2}{kTD}\kappa f(DTV) \tag{23}$$

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(6) Brönsted, *Z. physik. Chem.*, **100**, 139 (1922).

(7) In equation (15) R is the gas constant and is equal to 1.9885 cal. per degree; T is the absolute temperature, $\epsilon = 4.774 \times 10^{-10}$ is the charge on the electron; $z = z_1 = -z_2$ is the valence of the ions, which are equal in the case of a symmetrical valence type electrolyte such as zinc sulfate; $k = 1.372 \times 10^{-16}$ is the Boltzmann constant; D is the dielectric constant of the medium $= 78.54\ [1 - 0.00460\ (t - 25) + 0.0000088\ (t - 25)^2]$ for water according to Wyman [*Phys. Rev.*, **35**, 623 (1930)]; "a" is the ion size parameter of Debye and Hückel; $x = \kappa a$ where $\kappa^2 = -4\pi N\epsilon^2 \nu z_1 z_2 n/1000kTDV$; N is Avogadro's number $= 6.061 \times 10^{23}$; and n is the number of moles of electrolyte in V liters of solution.

(8) Bjerrum [*Z. physik. Chem.*, **119**, 145 (1926)] derived equation (16), but neglected the term containing dV/dT. Scatchard [THIS JOURNAL, **53**, 2037 (1931)] pointed out that this omission introduces an error of +7.2% in the case of water at 25°. The effect of thermal expansion is much less at lower temperatures, being only 1% at 12.5°. We use the following values for $TdV/3VdT$, 0 0256 at 25° and 0.0036 at 12.5°.

where

$$f(DTV) = 1 + 2\frac{T}{D}\frac{\mathrm{d}T}{\mathrm{d}D} + 5\left(\frac{T}{D}\frac{\mathrm{d}D}{\mathrm{d}T}\right)^2 + 2\frac{T^2}{DV}\frac{\mathrm{d}D}{\mathrm{d}T}\frac{\mathrm{d}V}{\mathrm{d}T} + \frac{2}{3}\frac{T}{V}\frac{\mathrm{d}V}{\mathrm{d}T} + \left(\frac{T}{V}\frac{\mathrm{d}V}{\mathrm{d}T}\right)^2 - 2\frac{T^2}{D}\frac{\mathrm{d}^2D}{\mathrm{d}T^2} - \frac{2}{3}\frac{T^2}{V}\frac{\mathrm{d}^2V}{\mathrm{d}T^2} \tag{24}$$

Randall and Rossini[9] derived an equation similar to (23) for the limiting slope of $\bar{c}_p - \bar{c}_p^{\circ}$ against $\sqrt{c}$. They, however, neglected the change of volume with temperature. Their equation contains an $f(DT)$ which is equal to our $f(DTV)$ after dropping all terms containing V and its derivatives. The value of $f(DTV)$ is 16% lower than the value of $f(DT)$ at 25°, so the effect of thermal expansion of the solution is even more important in the case of the heat capacity than in the case of the heat of dilution. For a 2–2 electrolyte at 25°, we obtain the following limiting expression valid for $C \longrightarrow 0$

$$\bar{c}_p - \bar{c}_p^{\circ} = 106\sqrt{c} \text{ at } 25^{\circ} \tag{25}$$

III. Computations

To evaluate these derivatives in equations (7) and (20), the smoothed values of $E^{\circ\prime}$ were expressed as fourth degree functions of the temperature.[10] The equations are of the form $10^5E^{\circ\prime} = A + BW + CW^2 + DW^3 + EW^4$ where $W = (t-25)/12.5$. The numerical values of the coefficients are given in Table II.

TABLE II

m	A	B	C	D	E
0	41086	−1402.5	−75.25	13.00	6.75
.0005	41724	−1351.9	−69.04	11.42	5.54
.001	41999	−1328.3	−65.75	10.33	4.75
.002	42365	−1297.8	−61.79	8.75	3.79
.005	42984	−1249.2	−52.50	6.17	1.50
.01	43531	−1211.2	−48.25	4.17	0.25

By use of these coefficients, the first derivatives are easily evaluated. $\bar{L}_2$ was computed only for the temperatures of 12.5 and 25° where the empirical formulas and the experimental measurements are most reliable for purposes of differentiation. For the same reason the second derivative and $\bar{c}_p - \bar{c}_p^{\circ}$ are calculated only at 25°. Our values of $-\Delta H$, $\bar{L}_2$, ΔC_p and $\bar{c}_p - \bar{c}_p^{\circ}$ are summarized in Table III.

Equation (20) yields ΔC_p for the process, which is equal to $\bar{c}_p$ ($ZnSO_4$,*m*) + C_p (Pb) − C_p (Zn) − C_p ($PbSO_4$). Using the value for E°, we can compute $\bar{c}_p^{\circ}$ for zinc sulfate when the heat capacities of the solids are known. From the "International Critical Tables" (Vol. V, p. 92) ΣC_p (solids) = −25.3 cal. per degree, whence

$$\bar{c}_p^{\circ}(ZnSO_4) = -132.4 - (-25.3) = -107.1 \text{ cal./degree/mole}$$

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(9) Randall and Rossini, THIS JOURNAL, **51**, 323 (1929).

(10) The Newton–Stirling central difference interpolation formula is a convenient method for obtaining these equations in a form symmetrical to 25°. See Whittaker and Robinson, "The Calculus of Observations," Blackie and Son, Ltd., 1924, equation A, p. 38.

TABLE III

SUMMARY OF COMPUTATIONS

F = 23063 cal./equivalent

m	$E^{\circ\prime}$	$10^3 \frac{dE^{\circ\prime}}{dT}$	$-\Delta H$	$\bar{L}_2$	$10^5 \frac{d^2E^{\circ\prime}}{dT^2}$	ΔC_p	$\bar{c}_p - \bar{c}_p^\circ$
			25°				
0	0.41086	−1.1220	34380	000	−0.9632	−132.4	0
.0005	.41724	−1.0815	34114	266	− .8840	−121.6	10.8
.001	.41999	−1.0627	33985	395	− .8416	−115.7	16.7
.002	.42365	−1.0382	33817	563	− .7909	−108.8	23.7
.005	.42984	−0.9993	33568	812	− .6720	− 92.4	40.0
.01	.43531	−0.9689	33402	978	− .6176	− 84.9	47.5
			12.5°				
0	0.42407	−0.9920	32630	000			
.0005	.43001	− .9612	32498	132			
.001	.43256	− .9479	32440	190			
.002	.43596	− .9305	32368	262			
.005	.44176	− .9053	32303	327			
.01	.44690	− .8825	32240	390			

In the absence of data on the heat capacity of zinc and lead both saturated with mercury we have employed values for the pure metals. The uncertainty in all probability is negligible for zinc but merits further investigation in the case of lead.

The calorimetric method of determining heats of dilution gives $L = n_1\bar{L}_1 + n_2\bar{L}_2$, the integral heat of dilution. In order to compare our results with those obtained in the calorimetric method, we have computed L by integrating graphically, using the formula $L = \int_0^{n_2} \bar{L}_2 dn_2$. The results are given in Table IV.

TABLE IV

THE INTEGRAL HEAT OF DILUTION OF ZINC SULFATE AT 25°

m	0.0005	0.001	0.002	0.005	0.01
L	157	246	366	571	739

IV. Discussion of Results

The values of $\bar{L}_2$ and $\bar{c}_p - \bar{c}_p^\circ$ are plotted against the $\sqrt{m}$ in Figs. 1 and 2. It is evident that $\bar{L}_2$ and $\bar{c}_p - \bar{c}_p^\circ$ are far from being linear functions of the square root of m even at concentrations as low as 0.0005 m. The figures emphasize what misleading results can be obtained by extrapolating linearly calorimetric data for high valence type electrolytes from concentrations as low as 0.01 m to zero concentration by means of the Debye–Hückel limiting slope.[11]

Randall and Rossini,[9] who first derived equation (23), employed E. Q. Adams' exponential representation of Kockel's data for D and computed

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(11) In a later paper we shall publish our development of the function for $\bar{L}_2$ on the basis of the Gronwall, La Mer and Sandved[4] extension of the Debye–Hückel theory and compare our results with this more complete expression.

$f(DT) = 1.75$, corresponding to a limiting slope for the partial molal heat capacity for a (2,–2) salt against $\sqrt{m}$ equal to 48 in place of our value of 106.

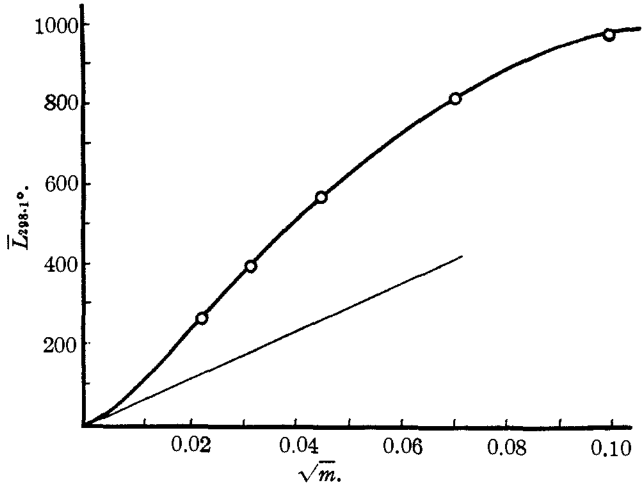

Fig. 1.—The partial molal heat content $\overline{L}_2$ of aqueous solutions of zinc sulfate at 298.1 °K. in calories per mole. The straight line represents the limiting law of the Debye–Hückel theory.

For the (1,–1) and (1,–2) salts, which they measured down to $m = 0.04$, they noted that the approximate limiting slopes of $\overline{c}_p - \overline{c}_p{}^0$ against $\sqrt{m}$

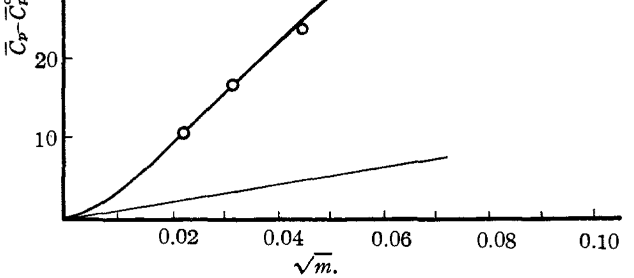

Fig. 2.—The influence of concentration upon the partial molal heat capacity of zinc sulfate in aqueous solution. The straight line represents the Debye–Hückel limiting law.

were 2 to 3 times that calculated by their formula, a difficulty which is now largely removed by the use of the Wyman formula, which yields

$f(DT) = 4.535$ and $f(DTV) = 3.802$. The computation of $\partial^2 E^{\circ\prime}/\partial T^2$ is so sensitive to experimental errors in $E^{\circ\prime}$ that it is possible that our values of the difference $(\bar{c}_p - \bar{c}_p{}^{\circ})$ may be subject to considerable error. On the other hand, we believe the form of the curve to be substantially correct.[12]

An indication of the reliability of our computed thermal quantities was obtained in the following manner: 0.02 mv., which was considered a reasonable estimate for the probable error of the *smoothed values* of $E^{\circ\prime}$, was alternately added to and subtracted from various combinations of successive temperature values of $E^{\circ\prime}$, at a given concentration. These changed values of $E^{\circ\prime}$ were expressed as a function of W and a new set of heat quantities calculated. This distortion of the function of $E^{\circ\prime}$ with respect to T made a difference of 0.1% in $-\Delta H$ and about 10% in Δc_p or $\bar{c}_p{}^{\circ}$, which appears to be the maximum limit of error for the postulated experimental precision. The reliability of $\bar{L}_2$ is therefore about (266 ± 34) or 13% at 0.0005 m and about (978 ± 33) or 3% at 0.01 m at 25°. The uncertainty in $\bar{L}_2$ at 12.5° is somewhat greater.

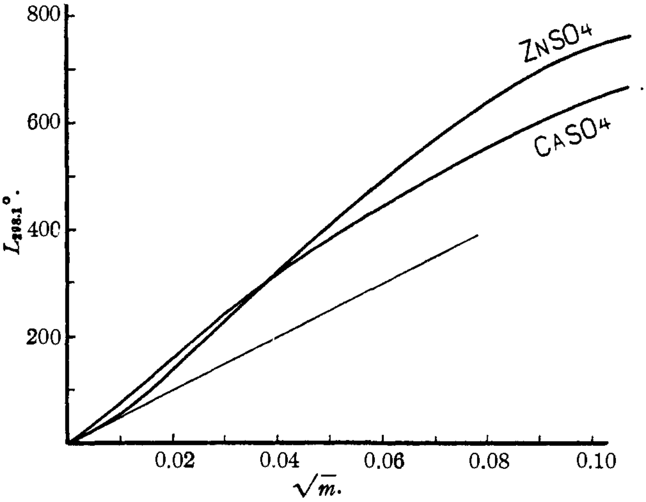

Fig. 3.—Comparison of the heat content of aqueous solutions of calcium sulfate determined calorimetrically by Lange and Monheim and of zinc sulfate determined from e. m. f. measurements by La Mer and Cowperthwaite. The straight line is the limiting law of the Debye–Hückel theory.

In Fig. 3 we have plotted the values of L ($ZnSO_4$) given in Table IV against the square root of m, along with the experimental values of L for calcium sulfate as determined by Lange and Monheim.[13] The data for zinc sulfate and calcium sulfate are very similar, as would be expected for

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[12] For a critical discussion of the extrapolation of heat capacity data see Gucker, Jr., and Schminke, THIS JOURNAL, **54**, 1358 (1932).

[13] Lange and Monheim, *Z. physik. Chem.*, [Abt. A] **150**, 349 (1930).

salts of the same valence type, but it is important to point out that in (2,–2) types the individual behavior has not vanished, a point which Lange[14] has repeatedly stressed. Since, as was demonstrated in the previous paper,[3] $\partial a/\partial T$ is zero for zinc sulfate, this individual behavior is most likely to be ascribed to the specific concentration dependence of D and perhaps of V, a problem which has not been satisfactorily investigated as yet for these salt solutions.

It is difficult to compare the reliability of the calorimetric method with the e. m. f. method since the former measures the integral heat of dilution whereas the latter measures the corresponding partial molal quantity. The smoothing of the experimental data which is a necessary preliminary to the numerical differentiation or integration of these quantities for purposes of comparison naturally obscures an answer to the question.

In the e. m. f. measurements the precision of $\bar{L}_2$ depends about equally upon the precision with which $(E^{\circ\prime}-E^\circ)$ and $d(E^{\circ\prime}-E^\circ)/dT$ can be measured since $E^{\circ\prime}$ is approximately equal to $T\ dE^{\circ\prime}/dT$ in the particular case of zinc sulfate.

There are no measured values of $\bar{c}_p{}^\circ$ for (2,–2) salts with which we may compare our result for zinc sulfate. Rossini[15] calculates values of -68.5 and -73.4 calories per degree per mole for calcium sulfate and barium sulfate, respectively, by combining data for other salts on the basis of the the additivity of ionic partial molal heat capacities at zero concentration. These figures are considerably less than our value. On the other hand, our value of -107 for the (2,–2) salt zinc sulfate is in better agreement with the dependence upon valence type since Randall and Rossini[9] and Rossini[15] find values of -15 to -30 for $\bar{c}_p{}^\circ$ of (1,–1) salts, and values of -50 to -70 for (1,–2) and (2,–1) salts.

Summary

1. Based upon electromotive force measurements of the cell Zn (satd. amalgam), $ZnSO_4(m)$, $PbSO_4(s)$, Pb (satd. amalgam) for the temperatures 0, 12.5, 25, 37.5 and 50° and the concentrations 0.0005, 0.001, 0.002, 0.005 and 0.01 m zinc sulfate the following values have been computed for the reaction Zn (s, satd. with Hg) + $PbSO_4(s) \longrightarrow ZnSO_4(m)$ + Pb (s, satd. with Hg) in the standard state of unit activity for $ZnSO_4$ at 298.1°K.

$E^\circ_{298.1} = 0.41086$ $\qquad -\Delta F^\circ_{298.1} = 18951$ cal.
$(dE^\circ/dT)_{298.1} = -0.0011220$ $\qquad -\Delta H^\circ_{298.1} = 34380$ cal.
$(d^2E^\circ/dT^2)_{298.1} = -0.000009632$ $\qquad -\Delta C^\circ_{p\,298.1} = 132.4$ cal./deg.

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(14) See Lange and Robinson, *Chem. Rev.*, **9**, 89 (1931), for an excellent summary of the work of Lange and collaborators on the calorimetric measurement of heats of dilution in dilute solution, and for a compilation of the temperature coefficients of the dielectric constant of water that can be calculated from the data of various investigators. Later papers by Robinson have appeared in THIS JOURNAL, **54**, 1311 (1932), and (with Hammerschmid), **54**, 3120 (1932).

(15) Rossini, *Bur. Standards J. Research*, **4**, 313 (1930); **7**, 47 (1931).

2. The partial molal heat capacity of zinc sulfate in the standard state (infinite dilution in water) is $\bar{c}_p{}^\circ$ $ZnSO_4 = -107$ calories per degree per mole.

3. The partial molal heat capacities, the relative partial molal and integral heat contents of zinc sulfate solutions have been computed at each concentration and the results compared with the theoretical formulas derived from the limiting forms of the Debye–Hückel theory using Wyman's determinations for the temperature dependence of the dielectric constant of water.

4. The contribution due to thermal expansion which has been neglected by previous investigators amounts to a correction of 16% at 25° in the theoretical limiting slope for the concentration dependence of the partial molal heat capacities.

5. The values for the integral heat of dilution of zinc sulfate are compared with the values for calcium sulfate as measured by Lange and Monheim for the same range of concentration. Aside from reasonable individual differences, which have been shown to persist to high dilution, the results are consistent with their valence type.

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[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF NORTHWESTERN UNIVERSITY]

The Heat Capacity and Related Thermodynamic Properties of Aqueous Solutions. II. Lithium and Sodium Hydroxides at 25°

BY FRANK T. GUCKER, JR., AND KARL H. SCHMINKE

Introduction

In order to widen the scope of our previous work, we have used the same methods to determine the specific heats of solutions of lithium and sodium hydroxides. The experiments were carried out in the Joule–Pfaundler *thermal balance*. In the *working calorimeter*, definite quantities, first of water and then of solution, were balanced against a fixed weight of water in the *tare* calorimeter. Using a multiple thermel, *temperature differences* were measured with a sensitivity of one or two hundred thousandths of a degree and specific heats were determined with an accuracy of about ±0.01%. The reader is referred to previous articles[1] for detailed descriptions of the apparatus and experimental technique.

Materials and Solutions

The hydroxides were prepared from the best available material, further purified in contact only with platinum, nickel or stainless steel.

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(1) Gucker and Schminke, THIS JOURNAL, **54**, 1358 (1932); Gucker, *ibid.*, **50**, 1005 (1928); Richards and Gucker, *ibid.*, **47**, 1876 (1925).