[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, COLUMBIA UNIVERSITY]

The Partial and Integral Heats of Dilution of Cadmium Sulfate Solutions from Electromotive Force Measurements[1]

BY VICTOR K. LA MER AND W. GEORGE PARKS

Introduction

In a previous paper[2] we reported electromotive force measurements for 0 and 25° on the cell

$$\text{Cd (2 phase amalgam), CdSO}_4\text{ (m), PbSO}_4\text{ (s), Pb (2-phase amalgam)} \qquad (1)$$

for which the cell reaction is

$$\text{Cd (s, satd. with Hg)} + \text{PbSO}_4\text{ (s)} = \text{CdSO}_4\text{ (m)} + \text{Pb (s, satd. with Hg)} \qquad (2)$$

By comparing the observed values of the activity coefficient, f, of cadmium sulfate which may be obtained from these measurements with the predictions of the theory of Gronwall, La Mer and Sandved[3] we found that the Debye–Hückel parameter "a" assumed the constant and physically plausible value of 3.6 Å. for both temperatures. From these data we reported preliminary values for the *mean* heat of dilution of cadmium sulfate for 12.5°.

To verify the important conclusion that $\partial``a"/\partial T$ is zero and to determine more precisely and more accurately the true heat of dilution of cadmium sulfate by considering the partial heat capacity of this salt, we have reinvestigated this cell for ten-degree intervals extending from 0 to 30° in the region of high dilution with improved apparatus for low temperature control. The theoretical treatment will follow closely the form presented in a recent paper by La Mer and Cowperthwaite[4] for the analogous cell involving the formation of zinc sulfate, from which the heat capacities and heats of dilution of this salt have been reported. We shall also reconsider our previous measurements in the light of Wyman's[5] improved values for the temperature coefficients of the dielectric constant of water which appeared after the computations in the previous paper had been completed.

Experimental

The measuring instruments, purification of materials, analytical technique and the method of filling and handling the electrode vessel have been described in detail previously.[2] An 11% by weight cadmium amalgam was employed since it has been shown by Jaeger and Steinwehr[6] in an investigation of the Weston standard cell that a 12.5%

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(1) The experimental work of this paper was performed by W. George Parks in 1930–1931 while Lecturer in Chemistry in Columbia University. He is at present Assistant Professor of Chemistry in the Rhode Island State College.

(2) La Mer and Parks, THIS JOURNAL, **53**, 2040 (1931).

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

(4) La Mer and Cowperthwaite, THIS JOURNAL, **55**, 1004 (1933).

(5) Wyman, *Phys. Rev.*, **35**, 623 (1930).

(6) Jaeger and Steinwehr, *Z. physik. Chem.*, **97**, 319 (1921).

amalgam showed no abnormal behavior on being cooled from 60 to 0°. Smith,[7] who studied amalgams containing from 1 to 20% cadmium, recommends a 10% amalgam as being stable between 51 and 0°. Vosburgh and Eppley[8] found the abnormally high electromotive force of standard cells after a decrease in temperature to be only temporary. Cohen and Kruyt[9] show a 10 and 12.5% amalgam to be normal at 0 and 25°.

A special thermostat which permits of rapid control of temperature was constructed of copper-lined Balsa wood. Cooling brine from a refrigerating unit operating at −15°. was circulated through copper coils at a rate depending upon the temperature desired. Alcohol was added to the bath liquid to prevent the formation of ice on the coils, which otherwise would interfere with precise temperature regulation. The temperature could be maintained to ±0.01° by thermostatic control with electric heaters. A special form of mercury regulator which facilitates rapid adjustment of temperature will be described in a separate note.[10] With this improved apparatus it was considered advisable to repeat the measurements previously made at 0°. In the earlier work 0° was obtained by an ice and water mush, and the temperature was lowered from 25 to 0° in one step. Lowering the temperature slowly by 10° intervals is believed to be a more reliable procedure.

A constant electromotive force was invariably obtained more rapidly by passing successively from higher to lower temperatures (twelve to eighteen hours) than by passing from lower to higher temperatures where approximately fifty hours were required. The saturation equilibrium for lead sulfate is attained more rapidly from supersaturation than from undersaturation, undoubtedly due to the slowness of the diffusion process in the latter case. In general the temperature level was established about 5 P. M. and the following day readings were made at intervals of an hour from 9 A. M. to 4 P. M. These values checked to within ±0.02 mv. Adjustment to a lower temperature level was then made and the procedure repeated. After the value at 0° had been established, measurements were made at ascending temperatures on the same cell over a three-day period at each temperature. Except in rare instances the second set of values checked the first within ±0.02 mv. The values of E, observed, recorded in Table I, represent the average of two cells. For $m = 0.02$ and $m = 0.002$ the average refers to three separate cells. The readings on different cells which are accepted checked each other within ±0.04 mv. The Leeds and Northrup type K potentiometer was calibrated by us in coöperation with Dr. MacInnes' staff at the Rockefeller Institute for Medical Research to the nearest 0.01 mv. We emphasize the importance of calibrating all potentiometers when using them for precision work. Two working standard cells, one immersed in a thermostat at 25° and the other in a room where the temperature always remained within the range of 22 to 27°, were employed. These cells were checked in this Laboratory and at the Rockefeller Institute at intervals against standard cells which had been certified recently by the Bureau of Standards.

Experimental Results

The method of correcting the experimental data given in Table I for the solubility of lead sulfate has been explained in detail in our first paper.[11] In Table II we give the numerical values of the coefficients in equation 4 [the Gronwall, La Mer and Sandved, eq. (107)] corrected to comply with Wyman's values for the dielectric constant of water, necessary for com-

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[7] Smith, *Phil. Mag.*, **19**, 250 (1910).

[8] Vosburgh and Eppley, THIS JOURNAL, **46**, 109 (1924).

[9] Cohen and Kruyt, *Z. physik. Chem.*, **65**, 359 (1909).

[10] W. G. Parks, *Ind. Eng. Chem., Anal. Ed.*, **5**, 357 (1933).

[11] La Mer and Parks, Ref. 2, p. 2049. (See Fig. 4.) The solubility data of Kohlrausch and Huybrechts and de Langeron are employed in our present calculations.

TABLE I

ELECTROMOTIVE FORCE OF THE CELL Cd-Hg (2-PHASE), $CdSO_4$ (m), $PbSO_4$ (s), Pb-Hg (2-PHASE) AT 0, 10, 20, 30°. COMPUTATION OF $E^{\circ\prime}$ AND E°

Molality $CdSO_4$	$E_{(\text{obs.})}$	$RT/n\mathbf{F}$ ln SO_4^-	$RT/n\mathbf{F}$ ln Cd^{++}	$E^{\circ\prime}$	$RT/n\mathbf{F}$ ln $f_{1,3,5}$ "a" = 3.6 A.	E°	Deviation from mean
			Temperature, 0°C.				
0.0005	0.20042	−0.08882	−0.08944	0.02216	−0.00558	+0.01658	+0.00002
.001	.18692	− .08109	− .08129	.02456	− .00798	.01658	+ .00002
.002	.17388	− .07307	− .07313	.02768	− .01118	.01650	− .00006
.005	.15796	− .06233	− .06235	.03328	− .01667	.01661	+ .00005
.01	.14648	− .05419	− .05419	.03810	− .02156	.01654	− .00002
.02	.13497	− .04603	− .04603	.04291	− .02686	.01605	
					Mean =	+0.01656	
			Temperature, 10°C.				
0.0005	0.20274	−0.09195	−0.09273	0.01806	−0.00589	+0.01217	+0.00005
.001	.18887	− .08403	− .08427	.02057	− .00843	.01214	+ .00002
.002	.17548	− .07574	− .07581	.02393	− .01182	.01211	− .00001
.005	.15896	− .06462	− .06464	.02970	− .01761	.01209	− .00003
.01	.14719	− .05617	− .05618	.03484	− .02273	.01211	− .00001
.02	.13547	− .04772	− .04772	.04003	− .02827	.01176	
					Mean =	+0.01212	
			Temperature, 20°C.				
0.0005	0.20277	−0.09496	−0.09599	0.01182	−0.00624	+0.00558	+0.00003
.001	.18865	− .08691	− .08724	.01450	−0.00894	.00556	+ .00001
.002	.17491	− .07838	− .07849	.01804	− .01253	.00551	− .00004
.005	.15799	− .06689	− .06691	.02419	− .01863	.00556	+ .00001
.01	.14588	− .05815	− .05816	.02957	− .02401	.00556	+ .00001
.02	.13402	− .04941	− .04941	.03520	− .02979	.00541	
					Mean =	+0.00555	
			Temperature, 30°C.				
0.0005	0.20168	−0.09808	−0.09928	0.00432	−0.00663	−0.00231	−0.00003
.001	.18724	− .08984	− .09023	.00717	− .00949	− .00232	− .00002
.002	.17313	− .08105	− .08117	.01091	− .01331	− .00240	+ .00006
.005	.15576	− .06917	− .06920	.01739	− .01976	− .00237	+ .00003
.01	.14341	− .06014	− .06015	.02312	− .02541	− .00229	− .00005
.02	.13152	− .05110	− .05110	.02932	− .03144	− .00212	
					Mean =	−0.00234	

puting the theoretical value of the activity coefficient given in column 6 of Table I. The quantities in Table I are defined by the equations

$$E_{(\text{obs.})} = E^\circ - \frac{\nu}{n}\frac{RT}{\mathbf{F}}\ln m - \frac{\nu}{n}\frac{RT}{\mathbf{F}}\ln f = E^{\circ\prime} - \frac{\nu}{n}\frac{RT}{\mathbf{F}}\ln f \tag{3}$$

$$\ln f = \frac{-\epsilon^2 z^2}{kTD_0 a}\,\frac{1}{2}\,\frac{x}{1+x} + \sum_{m=1}^{\infty}\left(\frac{\epsilon^2 z^2}{kTD_0 a}\right)^{2m+1}\left[\frac{1}{2}\ X_{(2m+1)}\ (x)_{-2m}\ \ Y_{2m+1}\ (x)\right] \tag{4}$$ [12]

TABLE II

NUMERICAL VALUE OF THE COEFFICIENTS IN THE GRONWALL, LA MER AND SANDVED EQ. (107), CORRECTED FOR WYMAN'S VALUES FOR THE DIELECTRIC CONSTANT OF WATER

t, °C.	D_0	$\frac{1}{2.3026}\,\frac{\epsilon^2}{2kTD_0} \times 10^8$	$\frac{1}{2.3026}\left(\frac{\epsilon^2}{kTD_0}\right)^3 \times 10^{21}$	$\frac{1}{2.3026}\left(\frac{\epsilon^2}{kTD_0}\right)^5 \times 10^{35}$
0	88.00	1.50093	0.143418	0.068520
10	84.12	1.51469	.147400	.071720
20	80.36	1.53147	.152352	.075781
30	76.75	1.55060	.158133	.080634

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(12) The numerical values of the universal constants are consistent with those employed by La Mer and Cowperthwaite, THIS JOURNAL, **53**, 4333 (1931), and Ref. 4.

The values for $E^{\circ\prime}$ for 0, 10, 20 and 30° are plotted as a function of $\sqrt{m}$ in Fig. 1. The straight lines represent the Debye–Hückel limiting law while the heavy lines correspond to the predictions of the extended theory for "a" = 3.60 Å. The deviations from the theoretical curve are not perceptible on this plot but their magnitude is represented by the deviations of the individually computed values for E° given in column 8 of Table I. Computations employing values of "a" equal to 3.64 and 3.56 Å. show that "a" = 3.60 Å. gives the best fit with the experimental data.

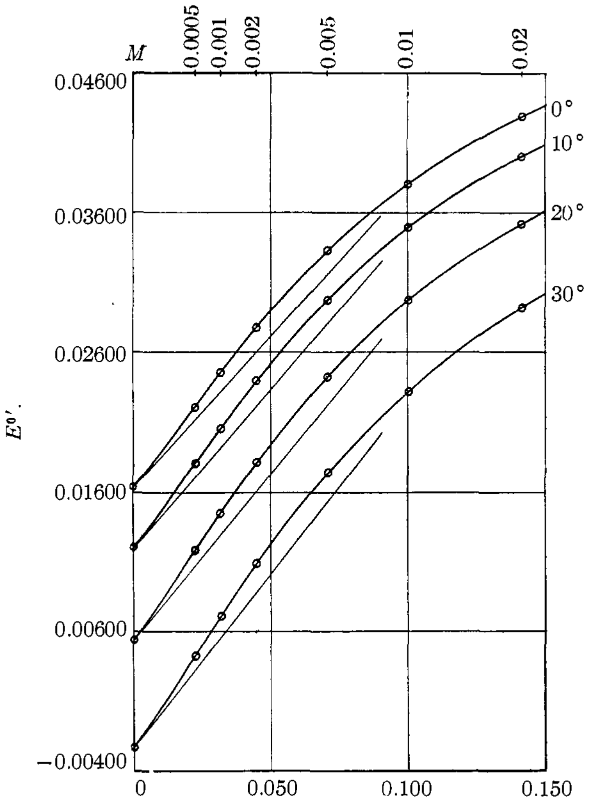

Fig. 1.

It will be noted that these deviations seldom exceed what might be attributed to experimental error at the temperature studied. It was our intention to extend our measurements to higher temperatures for a more extended test of the conclusion that $\partial``a''/\partial T$ is zero. Unfortunately, we find that at temperatures between 30 and 37° the electromotive force values become uncertain due undoubtedly to a transition in the solid cadmium.[13]

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(13) Cohen, "Physico-Chemical Metamorphosis and Problems in Piezochemistry," McGraw-Hill Book Co., Inc., New York, 1928, pp. 40–50; Getman, THIS JOURNAL, 39, 1806 (1917).

In our previous paper we found that "a" = 3.6 Å. gave the best fit for our data at 0 and 25° when Drude's value for D_0 is employed. The earlier data for 25° are recalculated in Table III using Wyman's value for D_0.

TABLE III

VALUES OF E_0 AT 25° "a" = 3.60 Å.

M	Drude D_0 = 78.77 Deviation from mean	Wyman D_0 = 78.54 Deviation from mean
0.0006070	−0.00010	−0.00005
.0007267	+ .00001	+ .00005
.0008675	− .00005	− .00002
.0009609	− .00004	± .00000
.0009819	− .00004	± .00000
.001077	− .00006	− .00003
.001119	+ .00001	+ .00004
.001332	− .00007	− .00004
.001993	− .00006	− .00004
.002994	− .00008	− .00008
0.003807	−0.00009	−0.00006
.004371	− .00003	− .00004
.005618	+ .00008	+ .00006
.007544	+ .00008	+ .00005
.007901	+ .00009	+ .00005
.008351	+ .00009	+ .00006
.009307	+ .00005	+ .00001
.009409	+ .00007	+ .00003
.01096	+ .00007	+ .00003

Mean (D) = +0.00142 ± 0.00006 (a. d.). Mean (W) = +0.00133 ± 0.00004 (a. d.)

When the results for $E^{\circ\prime}$ in column 5, Table I, are interpolated for 25° and compared with the previous work at 25° by interpolating graphically (Ref. 2, Fig. 5) to rounded molalities, we obtain the following differences between the two series for m = 0.000 to m = 0.02, namely: +0.06; −0.08; +0.01; −0.03; −0.02; +0.04; −0.07 mv. We consider this a satisfactory check on our work.

The best value of "a" is again 3.60 Å. Although the mean value of E° is reduced by 0.09 mv., it is gratifying to note that in this extensive series of measurements even better agreement with the extended theory is obtained by using Wyman's value instead of Drude's.

In Table IV we summarize the activity coefficients of cadmium sulfate calculated from the observed values of E and the mean value of E° given in Table I.

TABLE IV

THE ACTIVITY COEFFICIENTS OF $CdSO_4$

M	0°	10°	20°	30°
0.0005	0.788	0.784	0.780	0.775
.001	.712	.707	.702	.695
.002	.630	.616	.610	.602
.005	.491	.487	.478	.470
.01	.400	.394	.386	.377
.02	.326	.319	.309	.298

Heat of Dilution.—In Fig. 2 we plot the values of $E^{\circ\prime}$ given in Table I against the reciprocal of the absolute temperature. The slope of the curves at any point is a measure of the change in molal heat content, ΔH, of the cell process for the temperature and concentration of cadmium sulfate selected. Since the slopes change continuously it is evident that ΔH

varies considerably with temperature, which we shall show is due primarily to cadmium sulfate having a large negative value for its partial molal heat capacity. To detect changes in these quantities with changing concentration it is expedient to resort to numerical methods.

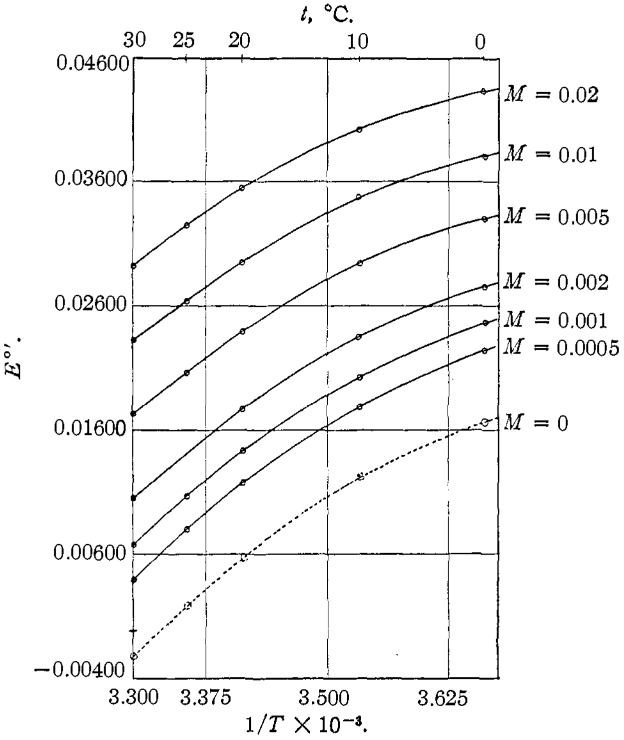

Fig. 2.

For purposes of computation La Mer and Cowperthwaite[4] showed that the Gibbs–Helmholtz equation assumes its most convenient form when written

$$-\Delta H = n\mathrm{F}[E^{\circ\prime} - T(\partial E^{\circ\prime}/\partial T)_P] \qquad (5)$$

By comparing the values for $-\Delta H$ at a finite concentration with the value for infinite dilution computed by setting $E^{\circ\prime} = E^{\circ}$, we can readily calculate $\bar{L}_2$, the partial molal heat of dilution of cadmium sulfate, by the equation

$$-\Delta H_{(m=0)} - (-\Delta H_{(m=m)}) = \bar{H}_2 - \bar{H}_2^0 = \bar{L}_2 \qquad (6)$$

corresponding to the process

$$\mathrm{CdSO_4}\,(m) = \mathrm{CdSO_4}\,(m = 0) + \bar{L}_2 \qquad (7)$$

In terms of the activity coefficient $\bar{L}_2$ can be written

$$\bar{L}_2 = -\nu RT^2\,(\partial \ln f/\partial T) \qquad (8)$$

Introducing the limiting law of the Debye–Hückel theory for $\ln f$, equation (8) takes the form

$$\bar{L}_2 = -{}^3/_4 \frac{\nu R \epsilon^2 z^2}{k D_0} \kappa \left(1 + \frac{T}{D_0} \frac{\partial D_0}{\partial T} + \frac{1}{3} \frac{T}{V} \frac{\partial V}{\partial T}\right)^{\text{[14]}} \qquad (9)$$

Having obtained $\bar{L}_2$ with the aid of equation (6) the integral molal heat of dilution of cadmium sulfate, L, was computed (Table VIII) according to the formula $L = \frac{1}{m} \int_0^m \bar{L}_2 \mathrm{d}m$. The limiting law for L is

$$L = V_m = -N \sum_{j=1}^{s} \frac{\epsilon^2 \nu_j z_j^2}{2D_0} \left[1 + \frac{\partial \ln D_0}{\partial \ln T} + \frac{1}{3} \frac{T}{V} \frac{\partial V}{\partial T}\right] \kappa \qquad (10)$$

When $\nu = 2$ the limiting slopes for $\bar{L}_2$ and L are given by the equations

$$\bar{L}_2/\sqrt{m})_{m \to 0} = -6N\epsilon^2 \frac{1}{D_0} \left[1 + \frac{\partial \ln D_0}{\partial \ln T} + \frac{1}{3} \frac{T}{V} \frac{\partial V}{\partial T}\right] \frac{\kappa}{\sqrt{m}} \qquad (11)$$

$$L/\sqrt{m})_{m \to 0} = \frac{-4N\epsilon^2}{D_0} \left[1 + \frac{\partial \ln D_0}{\partial \ln T} + \frac{1}{3} \frac{T}{V} \frac{\partial V}{\partial T}\right] \frac{\kappa}{\sqrt{m}} \qquad (12)$$

In Table V we give a summary of the numerical values to be used in equations 9, 10, 11 and 12. The values for the limiting slopes are in calories mole^{-1} $m^{-1/2}$.

TABLE V

CALCULATION OF LIMITING SLOPE FOR $\bar{L}_2/\sqrt{m}$ AND $L/\sqrt{m}$

t, °C.	D_0	$\frac{\partial D_0}{\partial T}$	$\frac{1}{3} \frac{T}{V} \frac{\partial V}{\partial T}$	$\left[1 + \frac{\partial \ln D_0}{\partial \ln T} + \frac{1}{3} \frac{T}{V} \frac{\partial V}{\partial T}\right]$	$\bar{L}_2/\sqrt{m}$	$L/\sqrt{m}$
10	84.12	−0.382	0.0012	−0.287	4410	2939
15	82.22	− .375	.0080	− .306	4830	3260
20	80.36	− .368	.0144	− .358	5789	3858

The change in heat capacity for the process, (2), can be calculated by the formula

$$\Delta C_p = n\mathrm{F}T(\partial^2 E^{\circ\prime}/\partial T^2)_p \qquad (13)$$

Computation of Thermal Quantities.—To reduce exaggeration of the experimental errors in the individual values of $E^{\circ\prime}$ in the differentiation process, we calculated values of $E^{\circ\prime}$ smoothed as a function of the concentration by the aid of equation 4. They differ from the experimental values by the amount given in the last column of Table I.

The smoothed values of $E^{\circ\prime}$ are then expressed as a polynomial of the third degree in terms of t°C., namely

$$E^{\circ\prime} = A + Bt + Ct^2 + Dt^3 \qquad (14)$$

The values of the coefficients in Table VI, therefore, represent all of the smoothed values as a function of the temperature, from which it is an easy matter to compute $(\partial E^{\circ\prime}/\partial T)_p$ and $(\partial^2 E^{\circ\prime}/\partial T^2)_p$ for substitution in equations 5 and 13.

The results of these calculations are given in Table VII for the temperatures 10, 15 and 20°, where the values of the derivatives will be most reliable.

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(14) See La Mer and Cowperthwaite, Ref. 4, page 1006, for the definition and the numerical values of the fundamental constants employed; also for the derivation of the equations of this section.

TABLE VI

NUMERICAL VALUE OF COEFFICIENTS × 10^6 FOR EQUATION 14

m	A	B	C	D
0.0000	1656	−31.0500	−1.470	0.013500
.0005	2214	−27.9500	−1.480	.014500
.001	2454	−26.7833	−1.450	.013833
.002	2774	−25.4000	−1.375	.011500
.005	3323	−22.1500	−1.415	.013000
.01	3810	−19.7833	−1.420	.013833
.02	4291	−16.0500	−1.425	.015000

TABLE VII

SUMMARY OF HEAT CALCULATIONS

m	ΔC_p	$-\Delta H_{\text{(process)}}$	$\bar{L}_2$
	10°		
0.0000	−278	7929	
.0005	−273	7782	147
.001	−270	7695	234
.002	−269	7566	363
.005	−268	7454	475
.01	−263	7361	568
.02	−255	7080	849
	15°		
0.0000	−229	9198	
.0005	−219	9016	182
.001	−219	8922	276
0.002	−227	8809	389
.005	−219	8676	522
.01	−212	8548	650
.02	−199	8217	981
	20°		
0.0000	−179	10,219	
.0005	−165	9980	239
.001	−168	9892	327
.002	−185	9843	376
.005	−172	9658	561
.01	−160	9479	740
.02	−142	9071	1148

The values of $\bar{L}_2$ and L for 15° are plotted against $\sqrt{m}$ in Fig. 3. The light lines correspond to the theoretical limiting slopes computed in Table V.

The concentration dependence of $\bar{L}$ and L has the characteristic form predicted by the theory of Gronwall, La Mer and Sandved up to 0.01 M. The more rapid increase of $\bar{L}$ above 0.01 M is in agreement with our previous data for 0 and 25° (Ref. 2, Fig. 8). A similar type of curve has been observed for hydrochloric acid by Rossini and by Harned and Ehlers.[15]

It is important to emphasize that aside from using the extended theory as the most legitimate means available for extrapolating for E° and for the very minor influence of smoothing the experimental data, a correction which is comparable in magnitude to the experimental error, the numerical values of L and $\bar{L}$ are the result of purely thermodynamic operations upon the experimental data and do not depend upon this theory. If desired, any influence which the extrapolation for E° may exert upon these quantities can be eliminated completely by taking the reference state as m = 0.0005 instead of infinite dilution.

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(15) Rossini, *Bur. Standards J. Research*, **9**, 499 (1933); Harned and Ehlers, THIS JOURNAL, **55**, 2179 (1933).

In Fig. 4 we plot the values of $E^{\circ\prime}_{(m)} - E^{\circ\prime}_{(m = 0.0005)}$ for the smoothed values and the corresponding smoothed values for zinc sulfate (Ref. 4, Table I) in order to compare the excess free energies of these two salts as a function of temperature. The differences are within experimental error at 0.001 and 0.002 molal but are of the order of 0.2 mv. at 0.01 molal, as would be expected since the "a" values differ perceptibly.

In Table VIII we give values of the integral heats of dilution for cadmium sulfate and zinc sulfate at 15°. These values were obtained by graphical integration using the formula $L = 1/m \int_0^m \bar{L}_2 dm$, and are in agreement with the values of the integral heat capacity difference per mole $(C_p - C_p^\circ)$ for zinc sulfate at 25° obtained by a similar integration of the $(\bar{C}_p - \bar{C}_p^\circ)$ values.

Unfortunately the e. m. f. measurements for cadmium sulfate could not be extended over as large a temperature range as in the case of zinc sulfate. The values of $(\bar{C}_p - \bar{C}_p^\circ)$ which could be computed from Table VII are consequently not sufficiently consistent to justify the calculation of heat capacity quantities for cadmium sulfate as a function of concentration. The values of L at 15° are larger for cadmium sulfate than for zinc sulfate in qualitative agreement with the recent calorimetric measurements of Plake.[16]

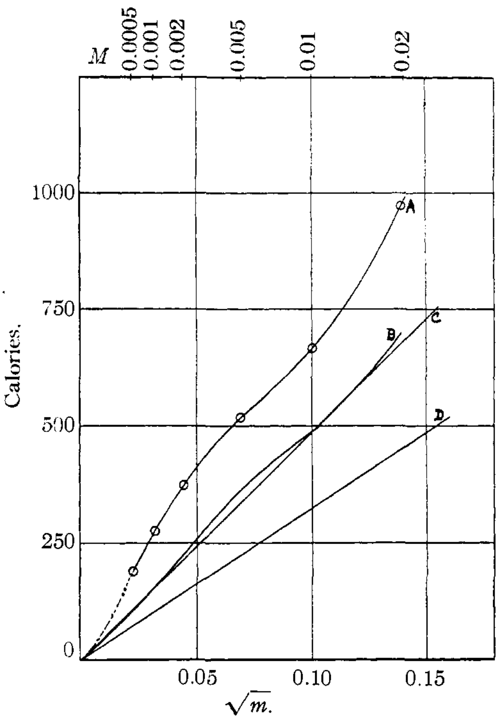

Fig. 3.—A = $\bar{L}_2$ ($CdSO_4$, 15°); B = L ($CdSO_4$, 15°); C = D.H.L.L. for $\bar{L}_2$ 15°; D = D.H.L.L. for L 15°.

TABLE VIII

MOLAL INTEGRAL HEATS OF DILUTION OF CADMIUM SULFATE AND ZINC SULFATE AT 15°

m	0.0005	0.001	0.002	0.005	0.01	0.02
$CdSO_4$ (15°)	99	158	249	378	483	642
$ZnSO_4$ (15°)	96	146	213	315	390	...
$ZnSO_4$ (25°)	157	246	366	571	739	...
$(C_p - C_p^\circ)$ $ZnSO_4$ (25°)	−5.8	−9.8	−15.2	−25.6	−35.1	...

We are indebted to Dr. I. A. Cowperthwaite for checking the graphical integrations

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[16] Plake, *Z. physik. Chem.*, **A162**, 257 (1932), p. 262.

The table illustrates how sensitive heats of dilution are to temperature and emphasizes the importance of comparing calorimetric measurements at a uniform temperature.

We do not claim that our computations of L and $\bar{L}$ are more accurate than those which can be obtained by the direct calorimetric methods now available. On the other hand, we are convinced that the values of "a" and of (∂"a"$/\partial T$) which can be computed from free energy measurements at different temperatures are superior in reliability to those values which can be calculated from calorimetric data by the use of the Lange–Meixner equation, even though the data are of high accuracy.

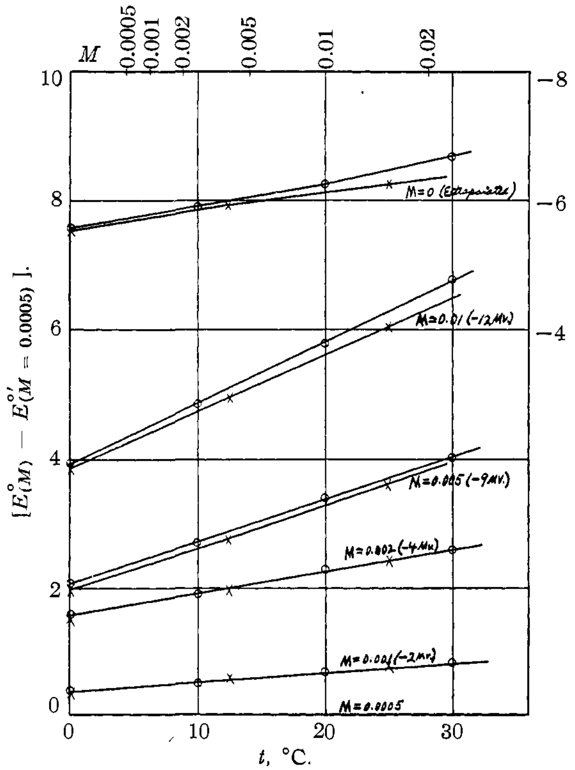

Fig. 4.—○, cadmium sulfate; ×, zinc sulfate.

In 1930–1931 Dr. I. A. Cowperthwaite and one of us, with the assistance of the late Dr. T. H. Gronwall, computed numerical tables of the first and second derivatives of the X_3 and X_5 functions which are required for computing $\bar{L}$ and $(\bar{C}_p - \bar{C}_p^{\circ})$ by the extended theory. Our object was to compare the theoretical predictions of the extended theory using values of "a" established from free energy measurements with the directly measured values of $\bar{L}$ and $(\bar{C}_p - \bar{C}_p^{\circ})$. This procedure would test whether or not the values of $(\partial D/\partial T)$ and $(\partial^2 D/\partial T^2)$ determined on pure water corresponded with those actually required by the experimental data at finite concentrations. Unfortunately we found that the contributions of the third and fifth approximations for $\overline{L}$ and $(\overline{C}_p - \overline{C}_p{}^\circ)$ in addition to being extremely sensitive to variations in "a" did not converge with sufficient rapidity for the range of "a" values given by the convergent equation 4 to be of any use for this purpose. In fact the very much simpler equation for the integral heat of dilution, L

$$L = -1196\,(Z^2/a)\,x/(1 + x) + 59.45\,(Z^2/a)^3\,(10^3X_3) + 29.64\,(Z^2/a)^5\,(10^5X_5) \quad (15)$$

valid for water at 25°,[17] which involves functions of the X type only, does not converge as rapidly for the same value of "a" as does equation 4 for log f which involves functions of the type $(^1/_2X_{2m+1} - 2mY_{2m+1})$. Table IX shows clearly the relatively greater importance of the third and fifth approximations for L as compared to log f. The third approximation contributes about one-half as much to log f as to L, whereas the fifth approximation contributes only one-third to one-seventh as much. The use of values of $(``a"/Z^2)$ other than 1 Å. will affect the rapidity of convergence but will not alter the relative importance of the third and fifth approximations for $L$ and log $f$ for the same value of $(``a"/Z^2)$. Our objections to "a" calculations from calorimetric data are based not only on the poor convergence and neglect of terms in $\partial V/\partial T$ in the Lange–Meixner equation but particularly to the uncertainty in the values of $(\partial D_0/\partial T)$,[18] which determine the coefficients in equation 15. The error produced by substituting $D = D_0$ is probably not very great, but we have no evidence as yet that $(\partial D/\partial T) = (\partial D_0/\partial T)$ for different salts at finite concentrations.[19]

TABLE IX

COMPARISON OF THE RAPIDITY OF CONVERSION OF THE EXTENDED THEORY IN TERMS OF LOG f (EQUATION 4) AND IN TERMS OF L (EQUATION 15) FOR $``a"/Z^2 = 1$ Å.; $T = 25°$; $D = 78.54$

	Percentage Contribution of Successive Terms					
	1st approximation		3rd approximation		5th approximation	
x	log f	L	log f	L	log f	L
0.01	94.65	88.56	3.35	5.85	1.99	5.61
.02	90.75	80.95	5.77	9.63	3.48	9.41
.05	84.01	66.88	10.13	17.04	5.87	15.11
.10	80.13	60.85	13.43	22.00	6.41	17.17
.15	79.94	60.24	14.72	24.15	5.33	15.62
.20	81.15	60.64	15.07	26.00	3.80	13.36
.25	82.82	62.67	14.88	26.83	2.30	10.50
.30	84.60	65.16	14.38	27.19	1.01	7.66

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[17] Derived by Lange and Meixner by a single temperature differentiation of the Gronwall, La Mer and Sandved free energy equation (29) and neglecting the temperature variation of V (*Physik. Z.*, **30**, 670 (1929), see p. 675).

[18] Lange and Robinson, *Chem. Rev.*, **9**, 89 (1931), where the values of various investigators are tabulated.

[19] La Mer, "Annual Survey of American Chemistry," Vol. V, 1930, pp. 12–13.

It is possible that the extended theory may not prove to be exact even when the higher approximations and the necessary dielectric data become available. In a recent note, Otto Halpern[20] claims that the statistical expressions for the average ionic potentials which are derived by the usual Debye method lead *in general* to expressions which do not obey the integrability relations of thermodynamics. This conclusion is necessary to explain the Gronwall[21] charging paradox. All expressions which contain *individual ionic diameters,* as well as higher approximations for ions of unsymmetrical valence type, do not conform to the integrability relations. Halpern's strictures would consequently invalidate all expressions based upon the Debye–Hückel theory of unsymmetric types and those for symmetric types in which the radius of the cation differs from that of the anion, except the limiting forms which are independent of "*a*." The numerical importance of these corrections is still unknown.

Summary

1. The electromotive force of the cell Cd (satd. amalgam, 11%) $CdSO_4$ (*m*), $PbSO_4$(s), Pb (satd. amalgam, 6%) has been measured at 0, 10, 20 and 30° for concentrations of cadmium sulfate of 0.0005, 0.001, 0.002, 0.005, 0.01 and 0.02 molal.

2. Using Wyman's value of the dielectric constant of water, and the Gronwall, La Mer and Sandved extension of the Debye–Hückel theory, the previous conclusion that "*a*" is 3.60 Å. for concentrations 0.0005 through 0.01 molal and independent of temperature from 0 to 30° is definitely confirmed.

3. The activity coefficients of cadmium sulfate are given for these concentrations and temperatures.

4. The following thermodynamic quantities have been computed for the process Cd(satd. Hg) + $PbSO_4$(s) = $CdSO_4$ (*m*) + Pb (satd. Hg) for the standard state of unit activity of cadmium sulfate for 15° (288.13°K.).

$E^\circ = 0.00905\ V$ $\Delta F^\circ = 417.6$ cal.
$(\partial E^\circ/\partial T)_p = -6.60 \times 10^{-4}$ $\Delta H^\circ = -9198$ cal.
$(\partial^2 E^\circ/\partial T^2)_p \cong -1.73 \times 10^{-5}$ $C_p^\circ \cong -229$ cal./deg.

5. The relative partial molal and integral heat contents of cadmium sulfate have been computed. Their concentration dependence is of the form demanded by the Gronwall, La Mer and Sandved theory. Exact comparison with the extended theory must await more precise determinations of the dielectric constant and its temperature derivatives at finite concentrations, as well as the calculations for the seventh and higher approximations for the calorimetric functions.

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(20) Halpern, *Phys. Rev.*, **43**, 495 (1933). Lars Onsager has independently reached a similar conclusion, *Chem. Rev.*, **13**, 73 (1933).

(21) Gronwall, La Mer and Sandved, Ref. 3, p. 367.

6. The partial molal heat capacity of cadmium sulfate is estimated to be approximately −200 cal./deg./mol. at 15°.

7. In the extended theory the equation for the activity coefficient converges more rapidly than the corresponding equation for the integral heat of dilution. Calculations of "a" based upon activity coefficients are consequently more reliable than those based upon equally accurate data of the heat of dilution.

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The Freezing Points of Aqueous Solutions. IV. Potassium, Sodium and Lithium Chlorides and Bromides

BY GEORGE SCATCHARD AND S. S. PRENTISS

The freezing points described in this paper were determined primarily as a part of a study of the freezing points of mixtures now being undertaken in this Laboratory.[1] They were made so early in order to give a comparison with the measurements on other salts, particularly the ammonium salts studied in our earlier paper; and to give a comparison of our temperature scale with that of other observers, most of whom have measured either potassium or sodium chloride. It is suggested that every freezing point apparatus be used to measure the freezing points of solutions of the easily purified potassium chloride; we believe in fact, that, for all but work of the very highest precision, the freezing point curve given in this paper would give a sufficient calibration in the range we have studied.

Recalibration of Apparatus.—In correlating the measurements previously reported[2] it was found that the precision of the measurements was about twice as good as anticipated for solutions more concentrated than 0.01 M, and that the greatest uncertainties lay in the purification of materials and the calibration of the apparatus. The apparatus was therefore carefully recalibrated. Although no change from our previous value was found greater than five hundredths of a per cent., the confirmation of our previous results warrants a brief description.

The resistance box used in the conductance measurements is frequently

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[1] The references to earlier measurements on these salts are given in "International Critical Tables," Vol. IV, pp. 258–259 and in reference 3. After these measurements were completed one of us (G. S.) had the opportunity of seeing in the thesis of Damköhler (Munich, under Professor Fajans) the results of measurements with LiBr, NaBr and KBr. Those with potassium and sodium bromides are related to ours very much as are those of Karagunis, Damköhler and Hawkinson with KCl, which were used by Damköhler to calibrate his thermocouple. The measurements with LiBr show an additional difference approximately linear in the concentration and equal to 0.005/M, our j values being more positive.

[2] Scatchard, Jones and Prentiss, THIS JOURNAL, **54**, 2690; Scatchard and Prentiss, *ibid.*, **54**, 2696 (1932).