JOURNAL OF THE AMERICAN CHEMICAL SOCIETY

VOLUME 55 DECEMBER, 1933 NUMBER 12

[CONTRIBUTION FROM THE LABORATORY OF PHYSICAL CHEMISTRY OF THE UNIVERSITY, ERLANGEN,[1] AND THE DEPARTMENT OF CHEMISTRY, UNIVERSITY OF PITTSBURGH]

The Heats of Dilution of Aqueous Solutions of Zinc, Cadmium and Copper Sulfates and Sulfuric Acid at 25°

BY E. LANGE, J. MONHEIM AND A. L. ROBINSON

Introduction

This paper presents data on the heats of dilution of aqueous solutions of zinc, cadmium and copper sulfates and sulfuric acid at 25°, obtained with a sensitive differential adiabatic calorimeter already described.[2] Previous papers of this series have been concerned with the thermochemical properties of very dilute solutions of 1-1, 2-1 and 1-2 valence types of strong electrolytes. The present measurements, together with those on magnesium and calcium sulfates,[2c] afford a comparison of the integral heats of dilution of a series of 2-2 type salts with a common ion.

From the integral heats of dilution, obtained by extrapolation to infinite dilution from the lowest measured concentration, relative partial molal heat contents have been calculated and have been compared in the case of zinc sulfate with values obtained from e. m. f. measurements of galvanic cells.[3]

The inclusion in the heats of dilution at very low concentrations of heat effects due to the displacement of the equilibrium $H_2O \rightleftharpoons H^+ + OH^-$ is pointed out and discussed briefly.

Finally, certain "residual thermodynamic effects"[4] are presented graphically for the case of zinc sulfate.

Experimental

The apparatus and detailed procedure have been fully described elsewhere.[2] The left and right halves of the calorimeter (including the pipet volumes) contained 1650 ± 2 and 1665 ± 2 cc. of water or solution, depending on whether a first or second dilution was being carried out. The pipets containing the solutions to be diluted had volumes of

---

(1) No. 39 in a series of Thermochemical Communications.

(2) (a) Lange and Monheim, *Z. physik. Chem.*, **149A**, 51 (1930); (b) Lange and Robinson, *Chem. Rev.*, **9**, 89 (1931); for further improvements see (c) Lange and Streeck, *Z. physik. Chem.*, **157A**, 1 (1931).

(3) Cowperthwaite, Thesis, Columbia University, New York City, 1930; La Mer and Cowperthwaite, THIS JOURNAL, **55**, 1004 (1933).

(4) Schottky, "Thermodynamik," Julius Springer, Berlin, 1929; Lange and Hammerschmid, *Z. physik. Chem.*, **160A**, 445 (1932).

24.16 ± 0.02 (left) and 24.41 ± 0.02 cc. (right). The end concentration of a first dilution from a given initial concentration was practically the same as the end concentration of a second dilution made from an initial concentration equal to one-half the first initial concentration (see Table I), thus permitting all data for a given electrolyte to be consistently plotted together and extrapolated to the reference state of infinite dilution.[5]

The zinc, cadmium and copper sulfates used were recrystallized de Haën preparations furnished with a certificate of guaranty; the sulfuric acid solutions were made up from a "Fixanal-Substanz" 0.1 N solution (de Haën). All solutions were prepared on a volume basis. To avoid possible heat effects caused by hydrolysis in the case of the zinc and cadmium sulfates[6] both the solutions to be diluted and the dilution water were slightly acidified with sulfuric acid (3×10^{-6} N).[7]

Results

The first two columns of Table I give the initial and end concentrations of a dilution, respectively. The third column of the table gives the heat effects of individual measurements and the fourth column gives the average of the individual measurements. In Fig. 1 the data of Table I are plotted against the square root of the molality (where necessary the concentrations given on a volume basis have been calculated to molalities using density data taken from "International Critical Tables" and the Landolt-Börnstein "Tabellen"). The individual points lie well on the smooth curves drawn and below values of $m^{1/2}$ of about 0.05 the curves are straight lines within the limits of the experimental error. The curves have been extrapolated linearly on the assumption that the observed slopes remain constant to infinite dilution.[8] This extrapolation permits the values of the integral

---

(5) Objections raised against the method of extrapolation [La Mer and Cowperthwaite, THIS JOURNAL, **54,** 4114 (1932)] were based on a misunderstanding and have been withdrawn [La Mer and Cowperthwaite, *ibid.*, **54,** 4754 (1932)].

(6) Dupont, *Compt. rend.*, **192,** 1643 (1931); Čupr, *Z. anorg. allgem. Chem.*, **198,** 310 (1931); Kolthoff and Kameda, THIS JOURNAL, **53,** 832 (1931); Denham and Marris, *Trans. Faraday Soc.*, **24,** 510 (1928).

(7) There is no reason to believe that the heats of dilution in pure water and in this very dilute sulfuric acid solution differ appreciably. The heats of dilution of potassium chloride in 15% aqueous sucrose solution and 5% aqueous urea solution [(Lange and Robinson, THIS JOURNAL, **52,** 4218 (1930)] differ only slightly from the values obtained in pure water despite the large differences that might be expected in view of the different dielectric properties of these solutions.

(8) That this assumption is subject to certain reservations is shown by measurements of E. Lange and H. Streeck now in progress. At very great dilutions the actual heats of dilution of salts seem to show an additional *positive* effect. Theoretically this effect is to be expected. The dilution water, assumed to be pure and neutral, contains a greater concentration of electrolyte after the dilution process than before. From the law of mass action $a_{H^+}a_{OH^-}/a_{H_2O} = K$ and since the activity of the water is practically constant at these very small electrolyte concentrations, it follows that $c_{H^+}\gamma_{H^+}c_{OH^-}\gamma_{OH^-} = k$. Since with increasing electrolyte concentration the activity coefficients ($\gamma_{H^+}\gamma_{OH^-}$) decrease, the ion product must increase so that, accompanying the exothermal dilution process, there is an endothermal dissociation of water. This is a typical "secondary salt effect." As long as the final salt concentration of a dilution experiment is greater than about 10^{-4} M this endothermal effect is negligible in comparison with the exothermal interionic effects. At greater dilutions, however, the amount of diluting water is so great and the interionic effect is so small that the increased dissociation of the water finally determines the sign and magnitude of the actual heat of dilution.

The displacement of the water equilibrium influences the actual heats of dilution of acids (or bases) to an even greater extent. Due to the repression of the ionization of the assumed pure and neutral diluting water by the acid solution being diluted a heat of neutralization is evolved. The effect is only about 1.4×10^{-3} calorie per liter of water but this is sufficient to cause a galvanometer deflection of about 2 mm. in the sensitive calorimeter used in these measurements. The effect was observed, but not accounted for, in some unpublished measurements of the heat of dilution of hydrochloric acid solutions heat of dilution for a given concentration to be read from the curves. The measured heats of dilution are of course so-called intermediate heats of dilution. It is estimated that the linear extrapolation introduces an uncertainty of ±5 calories into the values of the integral heat of dilution (excluding effects due to the displacement of the water equilibrium).[8] The

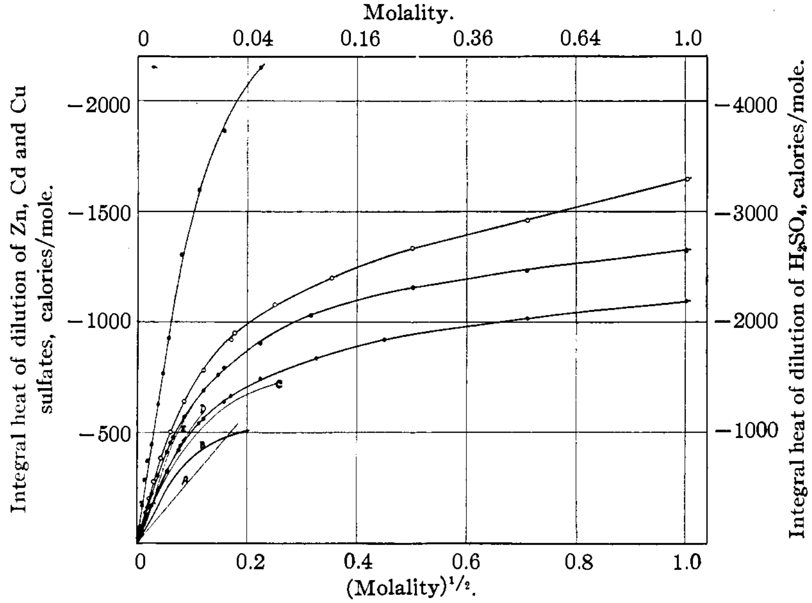

Fig. 1.—Integral heats of dilution at 25°: ○, $CdSO_4$; ◑, $CuSO_4$; ⊖, $ZnSO_4$; ●, H_2SO_4. A, Debye–Hückel limiting law; B, theoretical 2-2 type ("a" = 3.6 Å.), Lange–Meixner equation; C, $MgSO_4$; D, $CaSO_4$; E, $ZnSO_4$ (La Mer and Cowperthwaite).

reproducibility of the results is indicated in column 5 of Table I. Systematic errors entering into all the measurements are the usual errors of calorimetric procedure and are estimated to be less than 1% when the initial concentration of a dilution is greater than 0.00625 N and less than 1.5% for measurements starting at lower initial concentrations. Systematic errors due to adsorption processes have repeatedly been shown to be absent. The possibility of heat leakage through the short 1500 junction thermopile and its effect on the accuracy of the measurements have been considered[2a] in detail. To answer the objection that might be raised that the initial and final temperatures are not the same and that the measurements are not

by A. L. Robinson in 1930. Measurements with sulfuric acid solutions by J. Monheim with initial concentrations of $M/640$, $M/1280$ and $M/2560$ show an increasingly steeper course of the intermediate heat of dilution curve with increasing dilution with a slope several times as great as in the region of proportionality with $m^{1/2}$. These measurements are not included in Table I but will be referred to in a future publication which will also present the measurements of Lange and Streeck mentioned above.

The linear extrapolation of the curves of Fig. 1 probably represents therefore only that part of the actual (observed) heat of dilution for which the interionic forces are responsible.

TABLE I

MEASURED HEATS OF DILUTION AT 25°

Init. concn., mole/liter	End concn., mole/liter	ΔH, calories/mole individual meas.		Av. ΔH^c cal./mole
Zinc Sulfate				
1.0	0.01465	−641.5	640.3^b	641.7 ± 1.3^a
		640.2	644.6	
	0.02908	−518.5		518.5
0.5	0.007323	−668.0	668.0	668.0
	0.01454	−546.8	546.4	546.6 ± 0.2
0.2	0.002929	−714.2	712.2	713.0 ± 0.9
		711.4	714.0	
	0.005816	−599.5	597.6	598.3 ± 0.9
		596.8	599.4	
0.1	0.001465	−716.0	718.2	717.1 ± 1.1
	0.002908	−615.8	613.8	614.8 ± 1.0
0.05	0.0007323	−688.0	686.0	687.0 ± 1.0
	0.001454	−603.8	603.6	603.7 ± 0.1
0.025	0.0003661	−619.6	618.0	618.8 ± 0.8
	0.0007269	−561.2	558.8	560.0 ± 1.2
0.0125	0.0001831	−545.7	545.5	545.6 ± 0.1
	0.0003635	−502.3	506.2	504.2 ± 2.0
0.00625	0.00009153	−463.0	463.7	463.4 ± 0.4
	0.0001817	−422.2	428.8	425.5 ± 3.4
0.003125	0.00004577	−326.8	336.1	331.5 ± 4.6
	0.00009086	−330.3	325.4	327.9 ± 2.5
Cadmium Sulfate				
1.0	0.01465	−1041	1036	1039 ± 1.7
		1038	1041	
	0.02908	−868.4	875.4	871.9 ± 3.5
0.5	0.007323	−984.0	985.8	984.9 ± 0.9
	0.01454	−816.2	814.6	815.4 ± 0.8
0.25	0.003661	−1001	994	997.5 ± 3.3
	0.007269	−836.4	832.1	834.3 ± 2.2
0.125	0.001831	−988.0	979.2	983.6 ± 4.4
	0.003635	−838.6	832.6	835.6 ± 3.0
0.0625	0.0009153	−961.8	962.0	961.9 ± 0.1
	0.001817	−836.0	836.2	836.1 ± 0.5
0.03125	0.0004577	−891.6	900.6	896.1 ± 4.5
	0.0009086	−804.8	810.2	807.5 ± 2.7
0.01	0.0002634	−678		678
	0.000520	−603		603
Copper Sulfate				
1.0	0.01465	−764.4	763.5	764.1 ± 1.1
		766.2	762.4	
0.5	0.007323	−796.1	797.6	796.9 ± 0.7
	0.01454	−651.6	655.5	653.6 ± 1.9
	0.02165	−567.7	569.5	568.6 ± 0.9

TABLE I (*Concluded*)

Init. concn., mole/liter	End concn., mole/liter	ΔH, calories/mole individual meas.	Av. ΔH^c cal./mole
0.25	0.003661	−845.8 843.4	844.3 ± 0.9
		843.7	
	0.007269	−704.4 703.4	703.9 ± 0.5
0.1	0.001465	−869.6 871.4	870.5 ± 0.9
	0.002908	−743.4 741.4	742.4 ± 1.0
	0.004332	−661.6 661.4	661.5 ± 0.1
0.05	0.0007323	−816.4 816.6	816.5 ± 0.1
	0.001454	−718.4 720.6	719.5 ± 1.1
0.025	0.0003661	−757.7 755.4	756.9 ± 6.1
		768.2 746.2	
	0.0007269	−638.8 682.8	682.0 ± 8.0
0.0125		695.0 666.2	
	0.0001831	−670.4 662.0	666.9 ± 6.3
		668.4 667.8	
		680.8 651.8	
	0.0003635	−628.2 617.2	
0.00625		616.2 619.4	
		627.2 603.8	618.7 ± 6.0
	0.00009153	−544.0 548.0	553.3 ± 6.2
		562.3 558.9	
	0.0001817	−524.0 525.8	524.1 ± 2.4
0.003125		527.4 519.2	
	0.00004577	475 422 451	449 ± 17.9
	0.00009086	440 410 427	426 ± 10.1
		Sulfuric Acid	
0.05	0.0007323	−3417 3380	3410 ± 14.8
		3432 3412	
	0.001454	−3050 3027	3048 ± 9.2
		3058 3058	
	0.002164	−2781 2758	2770 ± 12
0.025	0.0003661	−3082 3089	3086 ± 3
	0.0007269	−2839 2832	2836 ± 3.5
0.0125	0.0001831	−2637 2609	2623 ± 14
	0.0003635	−2462 2442	2452 ± 10
0.00625	0.00009153	−2164 1945	2055 ± 110
	0.0001817	−1996 1875	1936 ± 60
0.003125	0.00004577	−1662 1760	1711 ± 49
	0.00009086	−1479 1554	1517 ± 38

[a] Probable error, exclusive of systematic errors. [b] Negative values denote heat evolved; these values are given with too great precision to facilitate the plotting of the data and the calculation of the probable error. [c] $-Vm_{\text{Anf}}m_{\text{End}}$ in the German papers of this series.

therefore truly isothermal, it may be pointed out that the construction of the calorimeter on the differential principle permits the compensation of any temperature change produced by the dilution process in one half of the calorimeter by electrical heating in the other half. The maximum temperature change produced by any of the dilution experiments for which data are presented in Table I was only about 0.014° (in most cases considerably less); since this is probably within the limit of ordinary thermostatic control the method might be referred to as "adiabatic-isothermal" calorimetry.[9]

In Fig. 1 are also shown the results of Lange and Streeck for calcium and magnesium sulfates. The results of La Mer and Cowperthwaite[3] obtained from the temperature coefficient of the e. m. f. of the cell Zn-Hg (two phase)/$ZnSO_4(m)$, $PbSO_4(s)$/Pb-Hg (two phase) are also represented graphically in Fig. 1.

In Table II are given the values for the integral heat of dilution of zinc, cadmium and copper sulfates (to $m = 1$) and sulfuric acid (to $m = 0.05$) as read from the extrapolated curves of Fig. 1. Considering the precision of the measurements, possible systematic errors and the error introduced by the extrapolation to infinite dilution it is estimated that these values are accurate to ±10 calories.

The relative partial molal heat contents of electrolyte and water ($\bar{L}_2$ and $\bar{L}_1$) have been calculated for the same concentration range from the expressions[10]

$$\bar{L}_1 = \frac{m^{3/2}}{2(55.508)} \frac{\mathrm{d}}{\mathrm{d}m^{1/2}} (\Delta H_\infty) \text{ and } \bar{L}_2 = -\Delta H_\infty - \frac{m^{1/2}}{2} \frac{\mathrm{d}}{\mathrm{d}m^{1/2}} (\Delta H_\infty)$$

TABLE II

INTEGRAL HEATS OF DILUTION AT 25°

		ΔH_∞,[a] calories/mole salt			ΔH_∞, calories/mole
(Molality)$^{1/2}$	$ZnSO_4$	$CdSO_4$	$CuSO_4$	(Molality)$^{1/2}$	H_2SO_4
0.01	− 76	− 110	− 97	0.01	− 327
.02	− 152	− 220	− 194	.02	− 655
.04	− 298	− 426	− 380	.04	−1304
.06	− 421	− 594	− 536	.06	−1946
.08	− 526	− 733	− 653	.08	−2510
.1	− 606	− 847	− 748	.1	−2960
.15	− 756	−1058	− 920	.12	−3300
.2	− 851	−1190	−1047	.14	−3580
.3	− 978	−1364	−1218	.16	−3815
.4	−1069	−1498	−1318	.18	−3997
.5	−1129	−1601	−1385	.20	−4150
.6	−1175	−1675	−1431	.22	−4272
.7	−1215	−1751	−1476		
.8	−1250	−1824	−1517		
.9	−1284	−1898	−1554		
1.0	−1314	−1973	−1590		

[a] $-Vm$ in the German papers of this series.

---

(9) Any changes in the heat of dilution due to these small temperature changes are negligible.

(10) Rossini, *Bur. Standards J. Research*, **6**, 799 (1931).

the required slopes being obtained graphically from a large scale plot of Fig. 1 or by the use of the Lagrange interpolation formula.[11] Table III gives the values of $\overline{L}_1$ and $\overline{L}_2$ so obtained and Fig. 2 shows a plot of these values against $m^{1/2}$.

TABLE III

RELATIVE PARTIAL MOLAL HEAT CONTENTS AT 25°

	$\overline{L}_1$[a] cal./mole H_2O				$\overline{L}_2$,[a] cal./mole electrolyte			
(Molality)$^{1/2}$	$ZnSO_4$	$CdSO_4$	$CuSO_4$	H_2SO_4	$ZnSO_4$	$CdSO_4$	$CuSO_4$	H_2SO_4
0.01	-0.0_468	-0.0_499	-0.0_488	-0.0_329	114	163	145	490
.02	$-.0_354$	$-.0_379$	$-.0_370$	−.0024	227	330	291	982
.04	−.0041	−.0064	−.0050	−.0176	440	607	553	1958
.06	−.0104	−.0142	−.0132	−.0615	620	825	746	2894
.08	−.0192	−.0276	−.0234	−.112	723	979	861	3478
.1	−.033	−.048	−.039	−.181	790	1111	965	3965
.12				−.230				4188
.14				−.314				4470
.15	−.066	−.101	−.085		918	1306	1150	
.16				−.376				4631
.18				−.449				4767
.2	−.117	−.188	−.165	−.497	1014	1420	1277	4840
.22				−.571				4928
.3	−.271	−.347	−.316		1145	1582	1410	
.4	−.416	−.62	−.47		1214	1712	1472	
.5	−.59	−.96	−.65		1256	1814	1522	
.6	−.79	−1.48	−.88		1301	1908	1573	
.7	−1.04	−2.22	−1.23		1342	2007	1618	
.8	−1.43	−3.28	−1.68		1380	2106	1668	
.9	−1.96	−4.72	−2.28		1424	2212	1721	
1.0	−2.76	−6.48	−3.25		1468	2333	1773	

[a] $\mathfrak{W}_1$ and $\mathfrak{W}_2$ in the German papers of this series.

Discussion

With the limits of experimental error the measured (intermediate) heats of dilution are proportional to $m^{1/2}$ below about 0.001 M. This proportionality (but not the value of the factor of proportionality) is in agreement with the limiting Debye–Hückel law. Although the extended theory[12] requires that the heats of dilution fuse into the limiting law straight lines at very low concentrations ($\Delta H_\infty = -2440\ c^{1/2}$ for 2–1 and 1–2 types and $-3765\ c^{1/2}$ for the 2–2 type) these measurements, which extend to 0.00005 M, give no definite indication of the "hump" found by La Mer and Cowperthwaite[8] for zinc sulfate and by La Mer and Parks[13] for cadmium sulfate at 12.5°. The data have therefore, as explained above,[8] been extrapolated linearly to infinite dilution. The individuality of the slopes persists to the lowest measured concentration; this has already been repeatedly

---

(11) Running, "Empirical Formulas," John Wiley and Sons., Inc., New York City, 1917.

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

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

emphasized for 1–1, 2–1 and 1–2 types of electrolytes.[14] The values of the slopes (below 0.001 *M*) are −32,700 for sulfuric acid, −10,800 for cadmium sulfate, −9500 for copper sulfate, −7500 for zinc sulfate and −7300 for calcium sulfate and magnesium sulfate.[2c] The limiting slope for sulfuric acid, if it is to be considered a 1–2 type electrolyte, is to be compared with the values found for the alkali sulfates,[2e] which range from −2200 for lithium sulfate to −1800 for cesium sulfate. It is quite possible that below 0.00005 *M* the individual curves fuse into the proper type curve but as far as the heats of dilution have been carried at present no definite confirmation of this suggestion has been found.

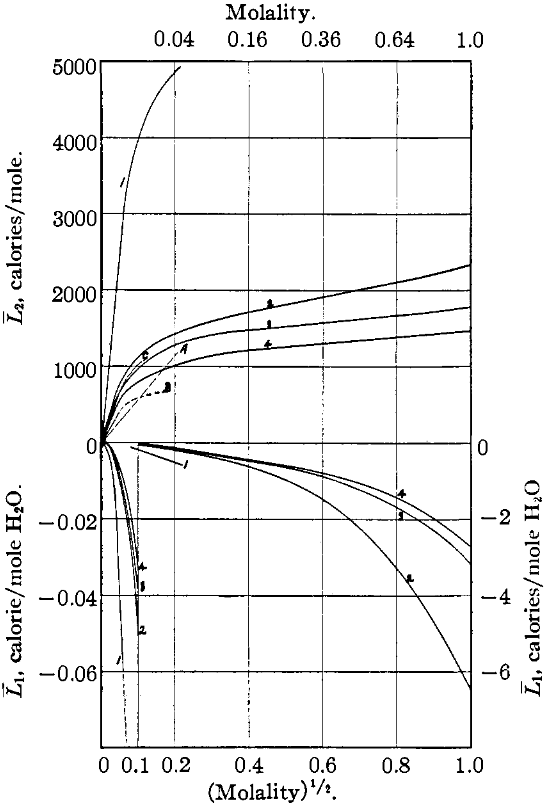

Fig. 2.—Relative partial molal heat contents at 25°: 1, H_2SO_4; 2, $CdSO_4$; 3, $CuSO_4$; 4, $ZnSO_4$. A, Debye–Hückel limiting law; B, theoretical 2-2 type ("*a*" = 3.6 Å.), Lange–Meixner equation; C, $ZnSO_4$ (La Mer and Cowperthwaite).

There are considerable differences between the values of ΔH_∞ and $\bar{L}_2$

---

[14] In general activity coefficients determined from freezing point or e. m. f. data do not show the same individuality or "degree of resolution" shown by the heats of dilution. This is perhaps partly because of the lower accuracy of the former type of measurement.

for zinc sulfate reported in this paper and those determined by La Mer and Cowperthwaite by application of the Gibbs–Helmholtz equation. A comparison of results reported in previous papers of this series with $\bar{L}_2$ values computed from e. m. f. measurements shows poor agreement in several other instances.[15] There is no theoretical ground for expecting the two methods to yield different results.[16] It is possible that the discrepancies are due to the usual difficulties encountered in obtaining accurate e. m. f. values in addition to the necessity for working over a wide temperature range and the uncertainty involved in the extrapolation from the lowest measured concentration (calorimetric measurements have been carried to lower concentrations) to infinite dilution.

In Fig. 1 the broken straight line represents the integral heat of dilution of a 2–2 type electrolyte as given by the limiting form of the Debye–Hückel theory.[17] Gatty[18] and Scatchard[19] have recently shown the necessity for the term in $\mathrm{d}V/\mathrm{d}T$.

$$\Delta H_\infty = \frac{0.239\ N^{3/2}\epsilon^3}{10^7\,D^{3/2}T^{1/2}}(\pi/1000\,k)^{1/2}(\Sigma\nu_i z_i^2)^{3/2}(1 + T/D\ \mathrm{d}D/\mathrm{d}T + T/3V\ \mathrm{d}V/\mathrm{d}T)c^{1/2}\ \text{cal./mole} \qquad (1)$$

Equation (1) becomes $\Delta H_\infty = -3765\ c^{1/2}$ for a 2–2 type electrolyte when Wyman's[20] data for the dielectric properties of water are used and the term in $\mathrm{d}V/\mathrm{d}T$ is placed equal to 0.015.[21] Figure 1 also shows the integral heat of dilution of a 2–2 electrolyte with an "a" parameter equal to 3.6 Å.[22] as computed from the equation of Lange and Meixner[23] which is based on the extended Debye–Hückel theory[12]

$$\Delta H_\infty = -\frac{1143\,z^2}{a}\,\frac{x}{1+x} + \frac{56.92(z^2)^3}{a^3}\,10^3X_3(x) + \frac{28.35(z^2)^5}{a^5}10^5X_5(x)\ \text{cal./mole} \qquad (2)$$

---

(15) Sodium chloride (e. m. f.) Harned and Nims, THIS JOURNAL, **54**, 423 (1932); (calorimetric) Robinson, *ibid.*, **54**, 1311 (1932), and Young and Vogel, *ibid.*, **54**, 3030 (1932); potassium bromide (e. m. f.), Pearce and Hart, *ibid.*, **43**, 2483 (1921), (calorimetric) Hammerschmid and Robinson, *ibid.*, **54**, 3120 (1932). A comparison of $\bar{L}_2$ values for cadmium sulfate at 12.5° in the concentration range 0.1–0.0005 M as determined by La Mer and Parks (e. m. f.), *ibid.*, **53**, 2040 (1931), and Plake (calorimetric), *Z. physik. Chem.*, **162A**, 257 (1932), also shows considerable differences.

(16) The relative partial molal heat contents of aqueous hydrochloric acid solutions as determined from the temperature coefficients of the cells $^1/_2H_2/HCl(m)/HgCl(s)/Hg$ [Ellis, THIS JOURNAL, **38**, 737 (1916)]; Noyes and Ellis, *ibid.*, **39**, 2532 (1917), agree with calorimetric measurements (Robinson, unpublished data) to better than one per cent. in the range 0.05–0.001 M.

(17) Debye and Hückel, *Physik. Z.*, **24**, 193 (1923).

(18) Gatty, *Phil. Mag.*, **11**, 1082 (1931).

(19) Scatchard, THIS JOURNAL, **53**, 2037 (1931).

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

(21) The term $T/3V\ \mathrm{d}V/\mathrm{d}T$ is an individual quantity (specific for each electrolyte) in an otherwise non-individual expression. However an inspection of the available data on the thermal expansion of 2–2 type electrolyte solutions (Landolt-Börnstein "Tabellen") shows that below 0.02 M the term has a value of 0.015 for magnesium sulfate, 0.0135 for zinc sulfate and 0.017 for copper sulfate so that a mean value of 0.015 can be used with sufficient exactness.

(22) This value of "a" has been selected for computation and plotting because La Mer and Cowperthwaite found "a" for zinc sulfate to be 3.64 Å. at 25° (in fact they found "a" to be practically temperature independent between 0 and 37.5°) and La Mer and Parks [THIS JOURNAL, **53**, 2040 (1931)] obtained a value of 3.6 Å. for cadmium sulfate (also from e. m. f. measurements).

(23) Lange and Meixner, *Physik. Z.*, **30**, 670 (1929).

In Equation (2) the coefficients have been calculated using Wyman's dielectric constant data.[24]

In Fig. 2 are also shown the limiting Debye–Hückel law for $\bar{L}_2$ of a 2–2 type electrolyte, $\bar{L}_2 = 5700\ c^{1/2}$,[25] and the partial molal heat content of a 2–2 type electrolyte with an "a" parameter equal to 3.6 Å.[26] and the results of La Mer and Cowperthwaite for $\bar{L}_2$ of zinc sulfate.

La Mer and Cowperthwaite and La Mer and Parks have interpreted e. m. f. measurements as indicating that $\mathrm{d}a/\mathrm{d}T$ is practically zero for zinc and cadmium sulfates. La Mer and Cowperthwaite[3] suggest that since $\mathrm{d}a/\mathrm{d}T$ is equal to zero, the individuality of the heats of dilution at low concentrations is to be attributed to the specific concentration dependence of D and perhaps V. Lange and Hammerschmid[4] have pointed out that the differences in the values of $T/3V\ \mathrm{d}V/\mathrm{d}T$ for salts of the same valence type cannot contribute more than one or two per cent. to the individuality of ΔH_∞ at low concentrations, an amount not detectable experimentally. Since La Mer and Cowperthwaite used the dielectric constant of pure water in their calculations of $\mathrm{d}a/\mathrm{d}T$ it is difficult to see how any conclusion can be drawn as to the specific concentration dependence of D and $\mathrm{d}D/\mathrm{d}T$ from the result $\mathrm{d}a/\mathrm{d}T = 0$, obtained with the above premise. The heats of dilution of potassium chloride in aqueous sucrose and urea solutions[27] differ only slightly from the values obtained in pure water in spite of the large differences that might be anticipated from a consideration of the different dielectric properties of these media. If reliable measurements of D and $\mathrm{d}D/\mathrm{d}T$ for electrolyte solutions were available it might be possible to estimate the contributions of these various specific factors to the individuality of the heats of dilution.

However, that the "a" values for zinc sulfate and cadmium sulfate are practically the same (3.64 and 3.6 Å.) as found by La Mer and Cowperthwaite and La Mer and Parks does not agree with our results. Assuming that $\mathrm{d}a/\mathrm{d}T$ is equal to zero and that D and $\mathrm{d}D/\mathrm{d}T$ are the same as for pure water both the Scatchard and Lange–Meixner equations applied to these measurements indicate that the "a" values for zinc sulfate and cadmium sulfate differ considerably at 25°. A rough computation shows that if the difference in the observed ΔH_∞ values for these two salts is to be attributed

---

(24) $x = \kappa a$, $\kappa = 0.329z\ c^{1/2}/10^8$ and the values for $X_3(x)$ and $X_5(x)$ have been taken from the tables prepared by Gronwall, La Mer and Sandved. The equation of Scatchard [Ref. 19 (equation (7), p. 2038)] containing the term in $\mathrm{d}\ \ln V/\mathrm{d}\ \ln T$ would give a curve lying slightly above the Lange–Meixner curve. The heat of dilution according to Scatchard has not been calculated since the difference between the values given by the two equations is probably less than 10%. Moreover, both equations converge rather poorly; the term in $X_5(x)$ contributes as much as 25% of the total to the calculated ΔH_∞ values (Lange–Meixner) at 0.002 M and $X_7(x)$ and $X_9(x)$ have not been computed.

(25) Bjerrum, *Z. physik. Chem.*, **119**, **145** (1926). This expression lacks the term in $\mathrm{d}V/\mathrm{d}T$ (Refs. 18, 19).

(26) $\bar{L}_2$ according to the Lange–Meixner equation has been calculated from the plot of ΔH_∞ (as calculated from equation (2)) against $m^{1/2}$, determining the slope of this curve and substituting in $\bar{L}_2 = -\Delta H_\infty - (m^{1/2}/2)(d/dm^{1/2})(\Delta H_\infty)$.

(27) Lange and Robinson, THIS JOURNAL, **52**, **4218** (1930).

solely to a difference in the "a" parameter then $a_{\mathrm{ZnSO_4}} - a_{\mathrm{CdSO_4}} \approx 1.5$ Å.

The observed initial slopes for the 2-2 type salts agree poorly with the value required by the limiting law. The agreement for 1-1, 2-1 and 1-2 types (except sulfuric acid) is much better.

According to the extended interionic attraction theory ΔH_∞ should be less negative as "a" increases in a series of electrolytes of the same valence type. If the values of "a" parallel the crystal radii of the variable ion in a series of salts with a common ion we should expect to find $a_{\mathrm{CaSO_4}} > a_{\mathrm{CdSO_4}} > a_{\mathrm{ZnSO_4}} > a_{\mathrm{MgSO_4}}$ with the position of $a_{\mathrm{CuSO_4}}$ uncertain.[28] On the basis of Equation (2) the results indicate $a_{\mathrm{CaSO_4,\, MgSO_4}} > a_{\mathrm{ZnSO_4}} > a_{\mathrm{CuSO_4}} > a_{\mathrm{CdSO_4}}$ below 0.001 M. The order of "a" as indicated by the heats of dilution of all 1-1, 2-1 and 1-2 type electrolytes investigated is that suggested by the order of the crystal ion radii. The order of the activity coefficients is not always the same.[29] The theoretical interpretation of this apparent anomaly is still obscure.

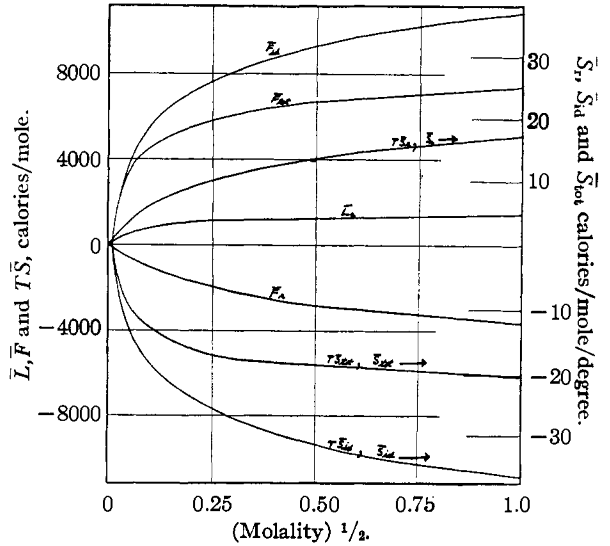

Fig. 3.—Partial molal quantities (real, ideal and total) of aqueous $ZnSO_4$ solutions at 25°.

In Fig. 3 are presented graphically the relative partial molal quantities $\bar{F}$, $\bar{S}$, $T\bar{S}$ and $\bar{L}$ for zinc sulfate for the concentration range of these measurements. The total partial molal quantities ($\bar{F}_{\mathrm{tot}}$, etc.) have been divided into their real ($\bar{F}_{\mathrm{r}}$, etc.) and ideal ($\bar{F}_{\mathrm{id}}$, etc.) parts, whereby[30]

---

(28) Goldschmidt, *Skrifter Norske Videnskaps-Akad. Oslo* **1**, *Mat-Naturv. Klasse*, 1926, No. 2; Pauling, THIS JOURNAL, **49**, 765 (1927).

(29) Lange and Streeck, *Naturwissenschaften*, **19**, 359 (1931).

(30) For a comparison of the terminology of this paper, which is that of Lewis and Randall ["Thermodynamics," McGraw-Hill Book Co., Inc., New York, 1923], and of the papers of this series published in German journals, which use the notation of Schottky,[4] see Lange and Hammerschmid.[4]

$$\bar{F}_{\mathrm{id}} = 2RT \ln m \qquad \bar{F}_{\mathrm{r}} = 2Rt \ln \gamma \qquad \bar{S}_{\mathrm{id}} = -2\mathrm{R} \ln m$$
$$\bar{S}_{\mathrm{r}} = 2RT\mathrm{d} \ln \gamma/\mathrm{d}\, T - 2R \ln \gamma \qquad \bar{L}_{\mathrm{r}} = \bar{L}_{\mathrm{tot}} = -2RT^2\mathrm{d} \ln \gamma/\mathrm{d}T$$

The $\bar{L}_{\mathrm{tot}} = \bar{L}_{\mathrm{r}}$ values are taken from Table III, the $\bar{F}_{\mathrm{r}}$ values are calculated from the activity coefficients (γ) determined by Bray[31] and the $\bar{S}_{\mathrm{r}}$ values are calculated from $\bar{S}_{\mathrm{r}} = (\bar{L} - \bar{F}_{\mathrm{r}})/T$. In Fig. 3 all total and ideal quantities are referred to the 0.0001 *M* solution. Of particular theoretical interest are the real quantities $\bar{L}$, $\bar{F}_{\mathrm{r}}$, $T\bar{S}_{\mathrm{r}}$ and $\bar{S}_{\mathrm{r}}$, amounts absorbed in the transfer of one mole of zinc sulfate from the reference state of infinite dilution to a real solution of given concentration. The possible physical processes which determine the sign and magnitude of these effects have been discussed elsewhere.[4]

The experimental part of this work was kindly aided by the Notgemeinschaft of the German Sciences.

Summary

The heats of dilution of aqueous solutions of cadmium, copper and zinc sulfates (from 1 *M* to 0.00005 *M*) and sulfuric acid (from 0.05 *M* to 0.00005 *M*) have been measured calorimetrically at 25° and extrapolated to infinite dilution to obtain integral heats of dilution.

Additional heat effects accompanying the dilution of very dilute electrolyte solutions due to the displacement of the equilibrium $H_2O \rightleftharpoons H^+ + OH^-$ have been discussed.

Relative partial molal heat contents and, for zinc sulfate, other related partial molal quantities (real and ideal) have been calculated for the concentration range of the measurements.

PITTSBURGH, PA.

RECEIVED APRIL 5, 1933
PUBLISHED DECEMBER 14, 1933

---

[31] Bray, THIS JOURNAL, **49**, 2372 (1927).