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THE ELECTROMOTIVE FORCE OF THE CELL  
 $\text{Zn(s)} \mid \text{ZnSO}_4(\text{m}) \mid \text{PbSO}_4(\text{s}) \mid \text{Pb(s)}$   
 AN EXPERIMENTAL DETERMINATION OF THE TEMPERATURE  
 COEFFICIENT OF THE ION SIZE PARAMETER IN THE  
 THEORY OF DEBYE AND HÜCKEL<sup>1</sup>

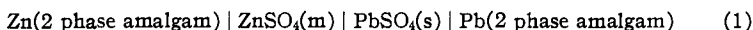
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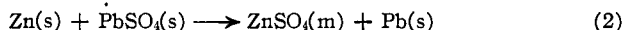
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Introduction

By determining precisely the e. m. f. of the cell



corresponding to the chemical reaction



at various temperatures and concentrations of zinc sulfate, we can compute the changes in free energy, heat content and heat capacities involved in this process. Of the components of this cell, zinc sulfate is the only one whose concentration is arbitrarily variable. Hence, if we can extrapolate our experimental determinations to obtain a sound value of  $E_0$ , we can compute the changes in the partial molal free energy, excess partial molal heat of transfer and excess partial molal heat capacity of zinc sulfate, as a function of concentration by using purely thermodynamic methods.

These thermal computations will be treated in detail in a following paper.

In this paper we report e. m. f. measurements on cell (1) for the concentrations 0.0005, 0.001, 0.002, 0.005 and 0.01  $M$  at the temperatures 0, 12.5, 25, 37.5 and 50°, and will compare these data with the predictions of the Gronwall, La Mer and Sandved<sup>2</sup> extension of the Debye-Hückel<sup>3</sup> theory. Our chief concern in this paper will be whether or not the value of the parameter " $a$ " introduced by Debye and Hückel as representing the distance of closest approach of the ions proves to be a physically reasonable and constant quantity when computed by the equation of Gronwall, La Mer and Sandved. If so, having such values at five different tempera-

<sup>1</sup> This paper is constructed from a dissertation entitled, "The Heats of Transfer and Partial Molal Heat Capacities of Zinc Sulfate in Aqueous Solution from the Temperature Coefficients of Galvanic Cells. An Application of the Extended Theory of Debye and Hückel" submitted in 1930 by Irving A. Cowperthwaite to the Faculty of Pure Science of Columbia University in partial fulfillment of the requirements for the degree of Doctor of Philosophy. The original manuscript was received for publication January 16, 1931; the delay in submitting the revised manuscript has been due in part to the absence of one of the authors on sabbatical leave.

<sup>2</sup> T. H. Gronwall, V. K. La Mer and K. Sandved, *Physik. Z.*, **29**, 358 (1928).

<sup>3</sup> P. Debye and E. Hückel, *ibid.*, **24**, 185 (1923).

tures, we may then obtain an unambiguous determination of the temperature coefficient of "a," a quantity of considerable theoretical importance in the interpretation of heats of dilution. The temperature coefficient of "a" obtained in this way we shall refer to as determined by direct experimental measurement.

### Theoretical

Debye and Hückel<sup>3</sup> introduce an approximation early in the development of their theory of solutions of strong electrolytes. For mathematical simplicity, they solved the Poisson equation by retaining only the linear term resulting from the expansion of the exponential in the Boltzmann expression for the density of electricity. Gronwall, La Mer and Sandved<sup>2</sup> criticize this procedure and point out that it frequently leads to error, particularly when dealing with high valence types, solvents of low dielectric constant, and electrolytes having a small value of the parameter "a." By solving the Poisson equation using the complete form of the Boltzmann expression, Gronwall, La Mer and Sandved obtain the following expression for the activity coefficient of an electrolyte of symmetrical valence type<sup>4</sup> where  $z_1 = -z_2 = z$ .

$$\log f = -\frac{\epsilon^2 z^2}{kTDa} \times \frac{1}{2} \times \frac{x}{1+x} + \sum_{m=1}^{\infty} \left( \frac{\epsilon^2 z^2}{kTDa} \right)^{2m+1} \left[ \frac{1}{2} X_{2m+1}(x) - 2m Y_{2m+1}(x) \right] \quad (3)$$

In this equation  $x = \kappa a$ , and  $\kappa^2 = \frac{8\pi N \epsilon^2 z^2 c}{1000 kTD}$ ,  $D$  is the dielectric constant of water,  $z$  is the valence of the cation and anion, "a" is the distance of closest approach of the two ions, and  $X(x)$  and  $Y(x)$  are known functions of  $x$ .<sup>4</sup>

Table I gives the numerical coefficients to be used with equation (3) to calculate  $-\log f$  through the fifth approximation at the temperatures studied.

Numerical values for the functions  $10^3 \left[ \frac{1}{2} X_3(x) - 2Y_3(x) \right]$  and  $10^5 \left[ \frac{1}{2} X_5(x) - 4Y_5(x) \right]$  have been tabulated by the authors for various assigned values of  $x$ . Values for these functions at any desired  $x$  may then be obtained from their tables by interpolation, thus rendering the application of equation (3) a relatively simple matter.

<sup>4</sup> The following numerical values of constants were used in the computations in this paper. The dielectric constant of water  $D = 78.54 [1 - 0.00460(t-25) + 0.0000088(t-25)^2]$  according to Wyman [Wyman, *Phys. Rev.*, **35**, 623 (1930)].  $N$  is Avogadro's number =  $6.061 \times 10^{23}$ ;  $k = 1.372 \times 10^{-16}$  is Boltzmann's constant;  $e = 4.774 \times 10^{-10}$  is the charge of an electron; and  $c$  is the concentration in moles per liter of solution.

TABLE I<sup>5</sup>

NUMERICAL VALUES OF COEFFICIENTS TO BE USED IN THE GRONWALL, LA MER AND SANDVED EQUATION

$t, ^\circ\text{C.}$	$\frac{\kappa}{z\sqrt{c}} \times 10^{-8}$	$\frac{1}{2.3026} \frac{e^2}{2kTD} \times 10^8$	$\frac{1}{2.3026} \left(\frac{e^2}{kTD}\right)^3 \times 10^{21}$	$\frac{1}{2.3026} \left(\frac{e^2}{kTD}\right)^6 \times 10^{42}$
0	0.3245	1.5009	0.1434	0.06852
12.5	.3264	1.5186	.1485	.07265
25	.3288	1.5407	.1551	.07809
37.5	.3315	1.5666	.1631	.08489
50	.3346	1.5963	.1725	.09322

A comparison of the first approximation and the extended theory shows that the additional terms of the latter are negligible in aqueous solution if  $z^2/10^8$  "a" is less than  $1/1.5 \text{ \AA}$ . But a discrepancy of increasing magnitude becomes important as "a" is assigned values less than  $1.5 \text{ \AA}$ . for a uni-univalent electrolyte or of less than  $6 \text{ \AA}$ . for a bi-bivalent type. The fact that the average diameters of most ions fall between the limits of  $1.5$  and  $6 \text{ \AA}$ . shows why the first approximation has so successfully accounted for the behavior of many uni-univalent electrolytes, while it has frequently given quite misleading results in the cases of higher valence types. The extended theory of Gronwall, La Mer and Sandved, by introducing terms in increasing powers of  $z^2/10^8$  "a," should thus be able to account for data on electrolytes involving small ions or solvents of low dielectric constant without necessitating Bjerrum's<sup>6</sup> additional assumption of partial association. It is important to note that the maximum percentage discrepancies between the two expressions occur in very dilute solution. The curve of  $-\log f$  against  $\sqrt{c}$  according to the extended theory has the limiting slope at extreme dilution (when  $x$  approaches zero), then curves up above a line representing the limiting slope through the origin, and at higher concentration crosses this line and then continues to fall away from the limiting slope with decreasing slope. The first approximation curve has the limiting slope at great dilution and then curves away with decreasing slope.

The electromotive force  $E$  of the cell in terms of its electromotive force  $E_0$  when the activities of the zinc and sulfate ions are one molal is related to the mean activity coefficient of the ions of the salt  $f = \sqrt{f_{Zn^{++}}f_{SO_4^{--}}}$  and to its molality  $m$  and number of ions  $\nu$  per molecule of salt as follows

$$E = E_0 - \frac{\nu RT}{nF} \ln m - \frac{\nu RT}{nF} \ln f \quad (4)$$

<sup>5</sup> Comparison of the coefficients in this table for the temperature of  $25^\circ$  with those given by Gronwall, La Mer and Sandved shows a slight difference. These authors base their calculations on the value of the dielectric constant for water given by Drude, whereas the above coefficients are computed on the basis of the more recent and better determinations of Wyman.<sup>4</sup>

<sup>6</sup> N. Bjerrum, *Det. Kgl. Danske Videnskab. Math.fys. Medd.*, **VII**, No. 9 (1926).

For convenience in plotting and calculating the mean activity coefficient, we shall calculate the value of the quantity  $E_0'$  defined by the equation

$$E_0' = E + \frac{\nu RT}{nF} \ln m \quad (5)$$

Combining this with (4) we obtain

$$E_0' = E_0 - \frac{\nu RT}{nF} \ln f \quad (6)$$

Assuming a value for the parameter " $a$ ," we may easily compute  $(\nu RT/nF) \ln f$  for each experimental point by means of equation (3). Substituting in (6) we obtain a value of  $E_0$  for each point. By successive approximations, we finally select a value of " $a$ " which will give a constant  $E_0$  throughout the range of concentration of legitimate applicability of equation (3). Thus we have a means of obtaining  $E_0$  giving all the experimental points equal weight without the necessity of placing undue emphasis on the most dilute determinations where the experimental difficulties are greatest.

We have given these well-known equations for electromotive force in detail to emphasize that we are following the procedure of Lewis and Randall<sup>7</sup> by defining them in terms of the molal (or  $m$ ) scale. On the other hand, the Debye-Hückel theory logically requires the use of the volume molar (or  $c$ ) scale in equation (3). Although the difference is completely negligible for these low concentrations at 0 and 12.5°, this is not necessarily true at the higher temperatures due to the decreasing density of the solutions. In our original computations<sup>1</sup> we employed the ( $m$ ) scale in equation (3). In the interests of greater formal rigor of computation, we have recomputed all of our theoretical values to the volume molar scale. As we expected, the recomputation is without influence upon the value of " $a$ ," but increases the value of  $E_0$  by 0.01 mv. at 25°, by 0.04 mv. at 37.5° and by 0.11 mv. at 50°. These corrections, it will be perceived, lie within the limits of experimental error claimed by us at these temperatures. We have discussed the results of these computations so that future workers in the field of highly dilute solutions at low temperatures may know the order of magnitude of the correction involved in interchanging concentration scales and thereby escape considerable laborious and unnecessary computation.

### Preparation of Materials

**Lead Nitrate.**—Baker and Adamson's best quality c. p. salt was recrystallized three times from boiling conductivity water. In each case the mother liquor was thrown off from the crystals by vigorous centrifuging.

**Zinc Sulfate.**—Kahlbaum's "for analysis" grade of zinc sulfate was recrystallized three times from boiling conductivity water. The crystals were filtered by suction and then further separated from the mother liquor by centrifuging. The final product was

<sup>7</sup> G. N. Lewis and M. Randall, "Thermodynamics," McGraw-Hill Book Co., Inc., New York, 1923.

dissolved in conductivity water, forming a stock solution of about 0.4 *M* concentration which was stored in a steamed-out Pyrex flask equipped with a siphon tube and an air inlet tube trapped with some of the same solution.

**Lead Sulfate.**—The lead sulfate was made as recommended by Bray.<sup>8</sup> It was precipitated from a 5% solution of the recrystallized lead nitrate by adding an excess of a 10% solution of zinc sulfate. The resulting solution with its precipitate was heated and boiled for fifteen minutes to coarsen the precipitate and permit it to assume a definite crystalline form. It was then washed ten times by decantation, and stored in a Pyrex flask under conductivity water till needed for electrodes.

**Mercury.**—Merck's redistilled mercury was stirred under a solution of mercurous nitrate and nitric acid for three days. It was distilled three times under 80 mm. of air and finally under high vacuum.

**Lead Amalgam.**—Sticks of Kahlbaum's lead "for analysis" were scraped clean from oxide, placed in a flask and sufficient mercury added to form a 6% amalgam. They were then sealed off under an atmosphere of nitrogen and heated in an oven to 125° with frequent agitation till a homogeneous single phase amalgam was formed. The flask was then opened and the amalgam filtered through capillary tubing into an evacuated flask where it was subsequently stored under a pressure of pure nitrogen. Such an amalgam is two phase through the temperature range of 0 to 50°, the solid phase being Pb<sub>2</sub>Hg. Puschin<sup>9</sup> found that all amalgams of between 1.8 and 66% of lead have the same electromotive force. Similarly Henderson and Stegeman<sup>10</sup> in their work found the same value for the electromotive force of any amalgam containing between 2.5 and 6% lead.

The lead and zinc used in this work were examined spectroscopically by Mr. Leo Shedlovsky at New York University and found to be without significant impurity.

**Zinc Amalgam.**—The zinc amalgam was made from sticks of Kahlbaum's "for analysis" grade zinc and purified mercury enough to form a 6% amalgam, by a procedure precisely similar to that described for the lead amalgam. According to the "International Critical Tables,"<sup>11</sup> a 6% zinc amalgam is two phase through the temperature interval from 0 to 50°.

**Nitrogen.**—Tank nitrogen was purified from oxygen by the wet combustion of copper using a modification of the method described by Van Brunt.<sup>12</sup> The absorption unit consisted of a tower 40 cm. long by 2 cm. in diameter containing copper turnings. Below the tower was a reservoir of 500-cc. capacity containing a solution made from equal volumes of a saturated solution of ammonium carbonate and strong ammonia. The incoming nitrogen operated a lift pump which circulated the solution over the copper. The nitrogen then passed slowly down over the wet copper, emerging near the bottom of the column. Two such towers were used in series. While the solution in the first unit turned deep blue, that in the second remained colorless. On opening the line and permitting access of oxygen to the second tower, its solution turned blue also. However, when the line was reformed and sufficient nitrogen passed through the system to circulate all the solution of the towers over the copper, the blue color of the solution in the second tower faded and completely disappeared as all the dissolved copper was reduced to the cuprous state. This observation would probably show that one such absorption unit was enough to remove all significant traces of oxygen. In fact Van Brunt claims to have obtained oxygen-free nitrogen by passing air through one such tower. The nitrogen passed from the second tower through two sulfuric acid scrubbers to remove am-

<sup>8</sup> U. B. Bray, *THIS JOURNAL*, 49, 2372 (1927).

<sup>9</sup> N. A. Puschin, *Z. anorg. Chem.*, 36, 210 (1903).

<sup>10</sup> W. E. Henderson and G. Stegeman, *THIS JOURNAL*, 40, 84 (1918).

<sup>11</sup> "International Critical Tables," Vol. II, p. 436.

<sup>12</sup> C. Van Brunt, *THIS JOURNAL*, 36, 1448 (1914).

monia, and then through a saturator containing zinc sulfate solution of the strength being studied.

### Experimental Method

Bray<sup>8</sup> made a detailed study of the lead-lead sulfate electrode and states that the following conditions are essential to reproducible results, namely: (1) oxygen must be excluded from the cell. (2) A definite crystalline form of lead sulfate is essential. (3) Equilibrium between the solid lead sulfate and the solution is best established before the electrode is made up. (4) The use of a two-phase amalgam is desirable.

In view of the conclusions of Bray, a new type of cell was developed permitting filling operations to be carried on out of contact with air, and allowing the cell when so filled to be completely sealed off under mercury. The cell contains no stopcocks or ground-glass joints with their possibility of air leaks.

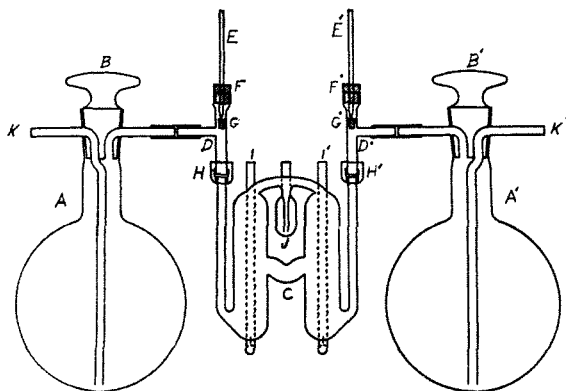


Fig. 1.

The cell and method of filling are illustrated in Fig. 1. The solution to be measured is divided into two parts. Half is put into flask A and to the other half is added a few grams of lead sulfate and the mixture put in flask A'. The flasks AA' are connected to the cell C by means of two T-tubes DD' which are connected to the cell C by short rubber connections buried under mercury in the mercury cups HH'. The upper ends of the T tubes DD' are closed by rubber stoppers FF' through which pass glass rods EE' on the lower ends of which are placed collodion-covered corks GG'. At the beginning of an experiment purified nitrogen is passed into the system through the tubes KK'. With the heads BB' of flasks AA' set in the indicated position, the nitrogen bubbles up through the solutions in the flasks AA' and passes over and through the cell C and then escapes through the mercury trap J. The nitrogen is run through the system for four hours to insure removal of all the oxygen from the solutions. The flask A' is shaken at frequent intervals to bring the lead sulfate into equilibrium with the oxygen-free solution. At the end of four hours the rubber stopper F is removed while a vigorous stream of nitrogen is running, and some zinc amalgam, which has been melted to a single phase, is run into the cell and then the stopper F is replaced. In an exactly analogous way, lead amalgam is admitted to the other leg of the cell through the T tube D'. Electrical connection between the amalgams and the external circuit is effected through platinum

wires sealed through the bottoms of the cell legs to the mercury contact tubes II'. As a precaution, the nitrogen is run through the system for another fifteen or twenty minutes after the amalgams are introduced to sweep out any trace of oxygen that might have entered the cell during the operation. Then the head B of flask A is given a quarter turn to stop the flow of nitrogen at that point. Flask A' is then shaken and its head B' given a half turn. Then the same pressure of nitrogen which has been used to sweep oxygen out of the solution now forces the solution and a suspension of lead sulfate over into cell C. This mixture is admitted up to the center cross tube of the cell. The glass rod E' is then pushed down, forcing the collodion-covered cork G' into the filling tube of the cell. If the T-tube D' is now removed, the mercury in the cup H' flows over the cork, completing the seal of the cell at that point. In a similar manner, the other leg of the cell is filled with pure zinc sulfate solution from the flask A to a level above the center cross tube, thus completing the circuit in the cell without the danger of solid lead sulfate getting over to the zinc amalgam, and the cell is again sealed off under mercury in the cup H. By this procedure, the cell is filled so that the amalgams come in contact only with solutions which have previously been freed of oxygen, and is a hermetically sealed portable unit. More mercury is added to the trap J and a cork is forced into the exit tube so that the cell can be observed through a range of temperature without danger of air being drawn in. Six such cells were made up for each concentration. For each experiment, the flasks and cells were first filled with hot chromic acid solution for a couple of hours, rinsed ten times with distilled water, allowed to stand with distilled water overnight, steamed out for an hour, set aside for a day filled with conductivity water, and finally dried in an oven at 125°.

The amalgams were made up out of contact with air and filtered through capillary tubing into evacuated flasks where they were subsequently stored under purified nitrogen at one and one-half atmospheres pressure. When the amalgams were required, the storage flasks were immersed in boiling water to melt the amalgams to a single phase. The amalgams were then forced out through capillary stopcocks drawing from the bottom of the mass so as to avoid any trace of oxide that might be floating on the surface.

The electromotive forces of the cells were measured in the following order: 25, 12.5, 0, 37.5 and 50°. The cells generally gave a constant e. m. f. at each temperature within two hours. The values for the six cells were generally grouped within the limits of 0.10 m.v., so that the average recorded value is probably better than 0.05 m. v.

Trouble was encountered measuring the 0.0005 *m* and 0.001 *m* cells at 50°. In those two cases the e. m. f.'s were not constant, but decreased steadily. Apparently zinc amalgam reacts with those very dilute solutions at elevated temperatures. This explanation was suggested by the appearance of a slight scum on the surface of the zinc amalgam. Scatchard and Tefft<sup>18</sup> studying the cell  $\text{Zn-Hg}(\text{two-phase amalgam})|\text{ZnCl}_2(m)|\text{AgCl}(s), \text{Ag}$  caused the zinc amalgam to react with the solution by introducing air at the interface. They observed a decrease in the electromotive force and the formation of scum on the amalgam surface.

The electromotive forces for 0.0005 *m* and 0.001 *m* at 50° were determined in two different ways. First the electromotive force was plotted against time and extrapolated to zero time. Figure 2 shows the e. m. f. of the 0.001 *m* cell at 50° plotted against time over a period of four days. The second method was to measure the cells at 25°, then to bring them to 50° holding them at that temperature till they showed a uniform rate of decrease and then bringing them back quickly to 25°. The two readings at 25° would not agree, and the discrepancy was ascribed to reaction in the cell at 50°. The difference between the two 25° readings was then added to the final 50° reading to get the true e. m. f. at 50°. The results of the two methods checked to  $\approx 0.1$  m. v., and we believe

<sup>18</sup> G. Scatchard and R. F. Tefft, *THIS JOURNAL*, 52, 2272 (1930).

that the e. m. f. at 50° is correct to that limit of error. At other temperatures and concentrations the precision is much better than this.

Considerable trouble was experienced from breaks which invariably occurred at the platinum seal in the zinc amalgam leg of the cell. When zinc amalgam is in contact with platinum, the zinc alloys with the platinum causing the latter to expand and break the seal. The Clark standard cell was discarded in favor of the Weston cadmium cell largely for this reason.<sup>14</sup>

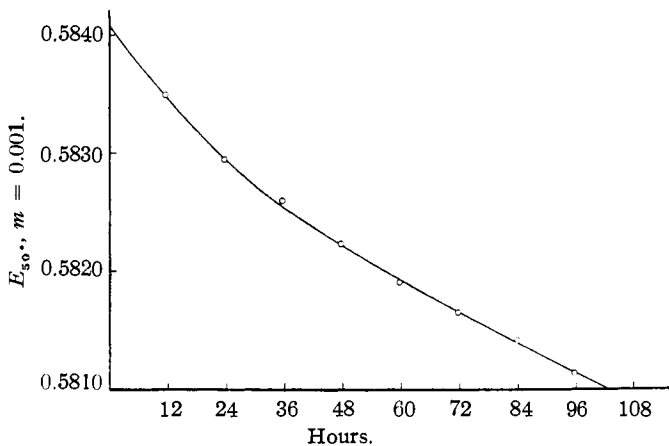


Fig. 2.

**Analysis of Zinc Sulfate Solution.**—The recrystallized zinc sulfate was dissolved in conductivity water to form a stock solution from which dilutions were made by weight. This stock solution was analyzed by two methods which checked closely. The first was to determine the zinc gravimetrically by the zinc ammonium phosphate method.<sup>15</sup> In the second method weighed samples of the solution were cautiously evaporated to dryness. The residue was treated with a few drops of strong sulfuric acid, the excess being driven off by heating in an air-bath, and finally weighed as zinc sulfate. Of the two methods, the latter was the more reproducible, the analyses frequently checking to 0.05% or better. The concentrations of all molal solutions are expressed as moles of zinc sulfate per 1000 g. of water, all weights being reduced to vacuum.

**The Apparatus.**—The measurements were made with a Leeds and Northrup Type K potentiometer which had been calibrated by Dr. L. G. Longworth of the Rockefeller Institute, and a Type R reflecting galvanometer number 2500 B. Owing to the low resistance construction of the cells used, no difficulty was encountered in obtaining unambiguous readings even with the most dilute solutions. An Eppley standard cell calibrated by the Bureau of Standards served as the standard cell.

Oil thermostat baths controlled by mercury regulators were used.

<sup>14</sup> E. C. McKelvey and M. P. Shoemaker, *Bull. Bur. Stand.*, **16**, 409 (1920).

<sup>15</sup> H. A. Fales, "Inorganic Quantitative Analysis," The Century Company, 1925.



Measurements below room temperature were made in thermostats equipped with brine coils. An excess of cooling was used and regulation accomplished by means of heaters. The temperatures of the baths were set by means of mercury thermometers which were compared with the laboratory standard, a platinum resistance thermometer calibrated by Dr. T. Shedlovsky of the Rockefeller Institute. The regulation of the baths was maintained to a precision of  $\pm 0.02^\circ$ .

TABLE II  
COMPUTATION OF  $E_0'$

Molality	$E$ (obs.)	$m \text{ SO}_4^{2-}$ from $\text{PbSO}_4$	$m \text{ SO}_4^{2-}$ total	$RT/nF \ln m \text{ SO}_4^{2-}$	$RT/nF \ln m \text{ Zn}^{++}$	$E_0'$
Temperature $0^\circ$						
0.0005	0.61980	0.0000272	0.0005272	-0.08882	-0.08944	0.44154
.001	.60627	.0000189	.0010189	-.08107	-.08129	.44391
.002	.59310	.0000101	.0020101	-.07307	-.07313	.44690
.005	.57705	.0000059	.0050059	-.06233	-.06235	.45237
.01	.56584	.0000043	.0100043	-.05419	-.05419	.45746
.02	.55559	.0000035	.0200035	-.04603	-.04604	.46352
.05	.54272	.0000030	.0500030	-.03525	-.03525	.47222
Temperature $12.5^\circ$						
0.0005	0.61600	0.0000348	0.0005348	-0.09271	-0.09354	0.42975
.001	.60236	.0000212	.0010212	-.08475	-.08501	.43260
.002	.58881	.0000133	.0020133	-.07640	-.07648	.43593
.005	.57214	.0000078	.0050078	-.06518	-.06520	.44176
.01	.56022	.0000058	.0100058	-.05666	-.05667	.44689
Temperature $25^\circ$						
0.0005	0.61144	0.0000434	0.0005434	-0.09656	-0.09763	0.41725
.001	.59714	.0000268	.0010268	-.08839	-.08873	.42002
.002	.58319	.0000168	.0020168	-.07972	-.07982	.42365
.005	.56598	.0000100	.0050100	-.06803	-.06806	.42989
.01	.55353	.0000075	.0100075	-.05914	-.05915	.43524
.02	.54252	.0000062	.0200062	-.05024	-.05025	.44203
.05	.52867	.0000056	.0500056	-.03848	-.03848	.45171
Temperature $37.5^\circ$						
0.0005	0.60519	0.0000531	0.0005531	-0.10037	-0.10172	0.40310
.001	.59078	.0000334	.0010334	-.09201	-.09245	.40632
.002	.57636	.0000212	.0020212	-.08303	-.08317	.41016
.005	.55862	.0000127	.0050127	-.07087	-.07091	.41684
.01	.54607	.0000096	.0100096	-.06162	-.06163	.42282
Temperature $50^\circ$						
0.0005	0.5992	0.0000636	0.0005636	-0.10415	-0.10582	0.3892
.001	.5841	.0000406	.0010406	-.09561	-.09617	.3923
.002	.56930	.0000260	.0020260	-.08634	-.08652	.39644
.005	.55096	.0000158	.0050158	-.07372	-.07376	.40348
.01	.53771	.0000121	.0100121	-.06410	-.06411	.40950
.02	.52603	.0000103	.0200103	-.05446	-.05446	.41711
.05	.51128	.0000098	.0500098	-.04170	-.04171	.42787

### Experimental Data

The observed values of the electromotive force ( $E$  obs.) and the computed function  $E_0'$  at the various concentrations and temperatures studied are tabulated in Table II. The values of  $E_0'$  there recorded are calculated so as to take into account the increase in sulfate-ion concentration due to the solubility of the lead sulfate.

The values of the solubility of lead sulfate at the temperatures in question were taken from the data of Böttger<sup>16</sup> and of Kohlrausch<sup>17</sup> as summarized by La Mer and Parks.<sup>18</sup> These values along with the activity coefficients computed from the first approximation of Debye and Hückel assuming " $a$ " = 3 Å., and the activity products are given in Table III.

TABLE III  
ACTIVITY PRODUCTS OF LEAD SULFATE

$t, ^\circ\text{C.}$	Soly. ( $m \times 10^4$ )	$f$	Activity prod. $\times 10^8$
0	1.08	0.913	0.972
12.5	1.24	.905	1.26
25	1.40	.898	1.58
37.5	1.57	.890	1.95
50	1.74	.881	2.35

The increase of sulfate-ion concentration due to the solubility of the lead sulfate was then computed in the following manner. Let  $x$  equal the activity of  $\text{Pb}^{++}$  and of  $\text{SO}_4^{--}$  from the solubility of lead sulfate,  $m$  equals the molality of zinc sulfate present, and  $f$  the activity coefficient of a bivalent electrolyte at molality  $m$  according to the Debye-Hückel first approximation assuming " $a$ " = 3 Å. Then

$$x(fm + x) = a_{\text{Pb}^{++}} a_{\text{SO}_4^{--}} = \text{constant} \quad (7)$$

We may solve for  $x$  and then calculate the molal solubility of lead sulfate in the presence of zinc sulfate at molality  $m$  by dividing  $x$  by  $f$ . If this value is then added to  $m$ , the total concentration of  $\text{SO}_4^{--}$  at the lead-lead sulfate electrode is obtained. We then get  $E_0'$  by adding  $(RT/nF) \ln m_{\text{Zn}^{++}}$  and  $(RT/nF) \ln m_{\text{SO}_4^{--}}$  (total) to the observed electromotive force  $E$  obs. as shown in Table II.

It is legitimate to use the first approximation of Debye and Hückel to compute the correction due to the solubility of lead sulfate because of its small magnitude. In order to demonstrate this, the correction at 50° was computed by means of a series of approximations using the extended theory and the values so obtained compared with those found by means of the first approximation equation. In this case, the two agreed within the experimental error, as is shown in Table IV.

<sup>16</sup> W. Böttger, *Z. physik. Chem.*, **46**, 604 (1903).

<sup>17</sup> F. Kohlrausch, *ibid.*, **64**, 129 (1908).

<sup>18</sup> V. K. La Mer and W. G. Parks, *THIS JOURNAL*, **53**, 2040 (1931).

TABLE IV  
CORRECTION OF  $E$  DUE TO SOLUBILITY OF LEAD SULFATE

$m$ ZnSO <sub>4</sub>	First approximation	G., L. and S. (5th approx.)
0.0005	1.67	1.71
.001	0.56	0.64
.002	0.18	0.18
.005	0.04	0.06
.01	0.01	0.02

The magnitude of the correction for the solubility of the lead sulfate increases rapidly with decreasing concentration and rising temperature. In the extreme case measured in this research, at  $m = 0.0005$  at  $50^\circ$ , the correction amounts to 1.67 mv. The values for the other temperatures can be found by taking the difference between columns five and six of Table II. Although this correction is undoubtedly a legitimate and sufficient procedure when its magnitude is small, nevertheless when the correction becomes large we are no longer dealing with a cell that is completely without transference. This restriction sets a lower limit to the concentration at which any cell of this type can be interpreted as a cell without transference.

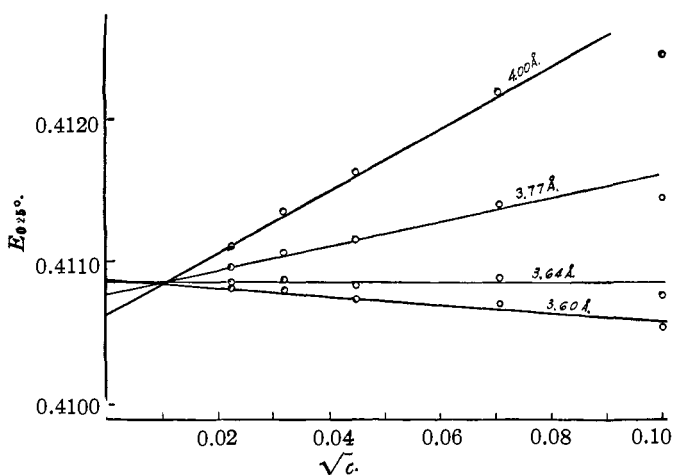


Fig. 3.

### Discussion of Results

Having values for  $E_0'$  in the concentration range where the Gronwall, La Mer and Sandved extension of the Debye-Hückel theory may be expected to be valid, we are in a position to compute  $E_0$ , the electromotive force of the cell with the zinc sulfate at activity 1  $m$ . Thus we assign arbitrary values to the parameter " $a$ " and compute the value of  $E_0$  corresponding to each experimentally measured value of  $E$ . The value of " $a$ " which yields a constant  $E_0$  throughout the concentration range at each temperature is accepted as the best value. The results of these computa-

tions at 25° are shown graphically in Fig. 3 where the calculated values of  $E_0$  for the different "a"'s are plotted against  $\sqrt{c}$ . Clearly the most constant value of  $E_0$  is obtained with "a" = 3.64 Å. at 25°.

Gronwall, La Mer and Sandved compute a value of "a" = 4.00 Å. for zinc sulfate from the measurements of Bray<sup>8</sup> on the same cell at 25°. The cause of this discrepancy between the two values for "a" may be traced back to the experimental measurements of the electromotive forces of the cells. The measurements obtained in this research deviate consistently from those of Bray in the most dilute solutions. In addition it should be pointed out that Gronwall, La Mer and Sandved obtained an "a" value of 3.60 Å. for zinc sulfate from the freezing point data of Hausrath.<sup>2</sup> They also found a value of 3.70 Å. for magnesium sulfate (a similar 2-2 electrolyte) from the freezing point data of Hall and Harkins.<sup>2</sup> La Mer and Parks<sup>18</sup> found a value of 3.60 Å. for cadmium sulfate from their measurements of the cell Cd-Hg (two-phase amalgam) | CdSO<sub>4</sub> | PbSO<sub>4</sub> | Pb-Hg (two-phase amalgam). The smaller value for "a" is not without precedent and conforms well with data on similar electrolytes.

Table V summarizes the calculated values of  $E_0$  at the different temperatures and for the best value of "a."

TABLE V  
SUMMARY OF VALUES OF "a" AND OF  $E_0$  AT THE TEMPERATURES STUDIED

<i>m</i>	<i>c</i>	$\kappa \times 10^{-8}$	$\alpha$	$E_0$	$\Delta$ from mean
<i>t</i> = 0°					
"a" = 3.64 Å.					
0.0005	0.00049996	0.014512	0.05282	0.43599	+0.00005
.001	.00099994	.020522	.07470	.43599	+ .00005
.002	.0019998	.029023	.10564	.43580	- .00014
.005	.0050000	.045889	.16704	.43584	- .00010
.01	.0100000	.064897	.23623	.43609	+ .00015
.02	.020001	.091781	.33408	.43688	+ .00096
.05	.050015	.145136	.52829	.43799	+ .00205
<i>t</i> = 12.5°					
"a" = 3.64 Å.					
0.0005	0.00049976	0.014596	0.05313	(0.42381)	-0.00026
.001	.00099954	.020641	.07513	.42411	+ .00004
.002	.0019990	.029186	.10624	.42404	- .00003
.005	.0049975	.046145	.16797	.42407	.00000
.01	.0099959	.065265	.23756	.42406	- .00001
<i>t</i> = 25°					
"a" = 3.64 Å.					
0.0005	0.00049856	0.014682	0.05344	0.41087	+0.00001
.001	.00099714	.020764	.07558	.41089	+ .00003
.002	.0019942	.029364	.10689	.41086	.00000
.005	.0049855	.046427	.16899	.41091	+ .00005
.01	.0099719	.065659	.23900	.41079	- .00007
.02	.019944	.092854	.33799	.41171	+ .00085
.05	.049866	.146822	.53443	.41294	+ .00208

TABLE V (Concluded)

$m$	$c$	$\kappa \times 10^{-8}$	$\alpha$	$E_0$	$\Delta$ from mean
$t = 37.5^\circ$					
$"a" = 3.60 \text{ \AA.}$					
0.0005	0.00049661	0.014772	0.05318	0.39618	-0.00010
.001	.00099324	.020898	.07523	.39640	+ .00012
.002	.0019864	.029551	.10638	.39626	- .00002
.005	.0049660	.046723	.16820	.39622	- .00006
.01	.0099320	.066077	.23788	.39634	+ .00006
$t = 50^\circ$					
$"a" = 3.73 \text{ \AA.}$					
0.0005	0.00049405	0.014876	0.05549	0.38195	+0.00003
.001	.00098810	.021038	.07847	.38194	+ .00002
.002	.0019762	.029752	.11098	.38187	- .00005
.005	.0049406	.047042	.17547	.38193	+ .00001
.01	.0098813	.066527	.24815	.38190	- .00002
.02	.019774	.094111	.35104	.38302	+ .00110
.05	.049410	.148763	.55490	.38450	+ .00258

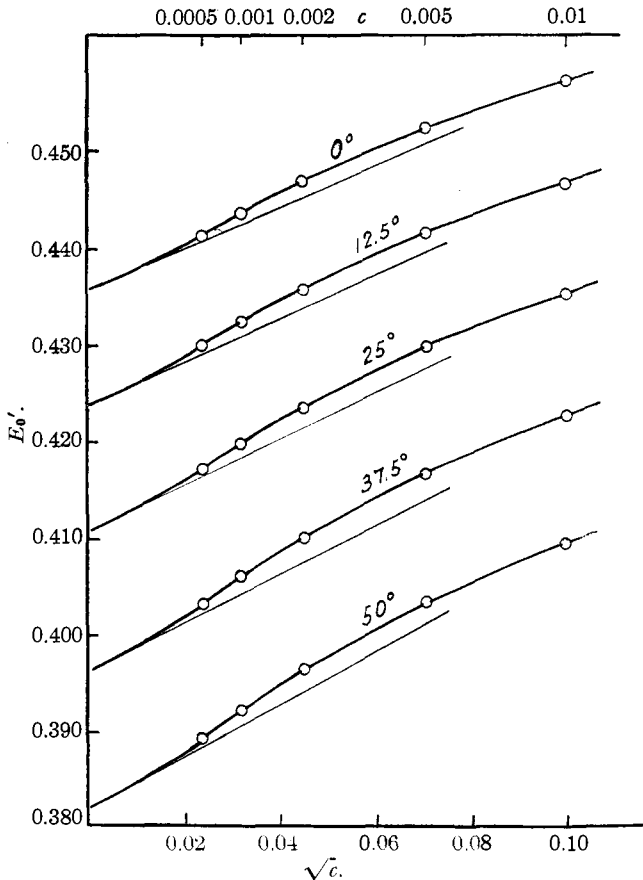


Fig. 4.

The values of  $E_0'$  with the values of  $E_0$  from Table V are graphically summarized in Fig. 4. Here the Debye-Hückel limiting slope for  $E_0'$  against  $\sqrt{m}$  is indicated by the straight line at each temperature. The experimental points correspond very closely to the heavy line which is the prediction of the Gronwall, La Mer and Sandved theory for the chosen value of "a." These curves show clearly how the extended theory deviates from the limiting law at great dilution (even at 0.0001  $m$  in the present example of a 2-2 electrolyte with "a" = 3.64 Å.).

The agreement of experiment and theory can be demonstrated even more strikingly by reversing these computations. Thus by assuming the best value of  $E_0$  from the previous calculations, we can compute the value of "a" for each experimental point. The results of such computations are shown in Table VI. For comparison, the ion size computed from the Debye-Hückel first approximation is also tabulated. The inadequacy of the first approximation to account for the data on zinc sulfate is quite apparent.

TABLE VI  
ION SIZE OF ZINC SULFATE

M	$t = 0^\circ$ $E_0 = 0.43594$		$t = 12.5^\circ$ $E_0 = 0.42407$		$t = 25^\circ$ $E_0 = 0.41086$		$t = 37.5^\circ$ $E_0 = 0.39628$		$t = 50^\circ$ $E_0 = 0.38192$	
	Debye	G. L. & S.	Debye	G. L. & S.	Debye	G. L. & S.	Debye	G. L. & S.	Debye	G. L. & S.
0.0005	-9.35	3.75	-10.59	3.45	-11.01	3.64	-11.83	3.53	-11.29	3.73
.001	-6.90	3.68	-7.91	3.66	-8.22	3.63	-7.87	3.68	-8.36	3.73
.002	-4.51	3.58	-5.31	3.63	-5.53	3.65	-6.03	3.60	-5.55	3.72
.005	-1.62	3.62	-2.20	3.64	-2.33	3.64	-2.65	3.59	-2.24	3.73
.01	+0.08	3.68	-0.24	3.64	-0.31	3.62	-0.53	3.61	-0.17	3.73

In Table VII are tabulated the theoretical values of the mean activity coefficient of zinc sulfate calculated according to equation (3), and also the observed values defined by equation (4).

TABLE VII  
ACTIVITY COEFFICIENT OF ZINC SULFATE

m	$t = 0^\circ$		$t = 12.5^\circ$		$t = 25^\circ$		$t = 37.5^\circ$		$t = 50^\circ$	
	Calcd.	Obs.	Calcd.	Obs.	Calcd.	Obs.	Calcd.	Obs.	Calcd.	Obs.
0.0005	0.790	0.789	0.785	(0.794)	0.780	0.780	0.772	0.775	0.769	0.768
.001	.714	.712	.708	.707	.701	.700	.690	.687	.687	.686
.002	.624	.627	.617	.617	.608	.608	.595	.595	.592	.593
.005	.495	.496	.487	.487	.478	.477	.463	.464	.461	.461
.01	.403	.400	.395	.395	.386	.387	.372	.371	.371	.371

We are now prepared to consider the principal question to be discussed in this paper, namely, the variation of "a" with temperature. The data of Table VI show that "a" is constant through the temperature interval from 0 to 37.5°. While the value at 50° is 0.1 Å. higher, this difference is small and may be due to the greater experimental difficulties encountered in making the measurements at 50°. Thus the value of "a" at this temperature should not be weighted as heavily as the values at the lower tempera-

tures. In any case we can state that  $d"a"/dT$  has been found to be equal to zero from 0 to 37.5° and that if deviations occur above that temperature, they are at least small. The data of this research and those of La Mer and Parks<sup>18</sup> are the only available *direct* tests of the constancy of "a" with temperature. These authors also found that "a" for cadmium sulfate is virtually the same at 0 and at 25°. The results of these two investigations therefore compel us to abandon the proposal of Gross and Halpern<sup>19,20</sup> and Bjerrum<sup>21,22</sup> that the specificity of heats of dilution may be ascribed to individual values of  $d"a"/dT$ , at least in the case of zinc and cadmium sulfates. Bjerrum's<sup>22</sup> statement that "a" is "stark-temperature empfindlich" is based upon the use of theoretical expressions for the heats of dilution obtained by employing only the first approximation of the Poisson and Boltzmann equations. By reference to Table VI it is clear that had we employed only the Debye approximation, we too would have obtained a negative value of  $d"a"/dT$ . From the data of cadmium sulfate and zinc sulfate it seems a fair presumption that the terms involving  $d"a"/dT$  in the expression for heats of dilution are quite negligible in dilute solution and that an explanation of specificity in the thermal equation of state must be sought in other directions than specificity in the temperature coefficient of "a."

The reason that the values of  $d"a"/dT$  and even "a" are relatively less certain when evaluated by the use of calorimetrically determined heats of dilution in contrast to the direct determination of "a" and  $d"a"/dT$  from free energy measurements at different temperatures, as carried out in this present paper, is that the theoretical formula for heats of dilution contains  $dD/dT$  as a general multiplicative factor the value of which is not as definitely established as is that for  $D$ .<sup>23,24</sup> In the absence of reliable values for  $dD/dT$ , it is customary to fit the calorimetric data by adjusting both  $d"a"/dT$  and "a." It is obvious that the procedure we have employed, namely, direct determination of "a" in the free energy formula for each temperature, obviates these uncertainties and difficulties as neither  $d"a"/dT$  nor  $dD/dT$  enter into the formulas employed.

Professor H. C. Urey has pointed out that the distance between the center of a zinc ion and a hexavalent sulfur ion with one oxygen ion on the line of centers between may be obtained from the tables given by V. M. Goldschmidt.<sup>25</sup> It equals 3.83 Å. (Pauling) or 3.81 Å. (Goldschmidt).

<sup>19</sup> P. Gross and O. Halpern, *Physik. Z.*, **26**, 403 (1925).

<sup>20</sup> P. Gross, *Monatsh.*, **48**, 243 (1927).

<sup>21</sup> N. Bjerrum, *Trans. Faraday Soc.*, **23**, 445 (1927).

<sup>22</sup> N. Bjerrum, *Ber.*, **62**, 1091 (1929).

<sup>23</sup> E. Lange, *Z. Elektrochem.*, **36**, 772 (1930).

<sup>24</sup> E. Lange and A. L. Robinson, *THIS JOURNAL*, **52**, 2811 (1930); for corrections see *Chem. Rev.*, **9**, 89 (1931), pages 91-92.

<sup>25</sup> Goldschmidt, *Trans. Faraday Soc.*, **25**, 253 (1929), see page 282.

The corresponding values for  $\text{CdSO}_4$  are 4.06 Å. (Pauling) or 4.01 Å. (Goldschmidt). These values represent maximum distances between the centers. The distance of closest approach of the centers of the zinc and sulfate ions would be somewhat smaller depending upon the particular configuration chosen for the system.

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### Summary

Electromotive force measurements precise to  $\pm 0.05$  mv. are reported for the cell  $\text{Zn}$  (two phase amalgam) |  $\text{ZnSO}_4(m)$  |  $\text{PbSO}_4(s)$  |  $\text{Pb}$  (two phase amalgam) for the molalities 0.0005, 0.001, 0.002, 0.005 and 0.01  $m$  and at the temperatures 0, 12.5, 25, 37.5 and 50°; also at 0.02 and 0.05  $m$  at 0, 25 and 50°.

The measurements are in excellent agreement with the requirements of the Gronwall, La Mer and Sandved extension of the Debye-Hückel theory. The extended theory yields a physically reasonable value for the ion size parameter " $a$ ," which is constant throughout the 20-fold concentration range 0.0005 to 0.01  $m$ , while the first approximation gives physically absurd negative values which change rapidly throughout the same concentration range. The value of  $E_0$  calculated by means of the extended theory at each temperature is constant throughout the range from 0.0005 to 0.01  $m$ .

The mean activity coefficients for zinc sulfate have been computed and compared with the observed values for the temperatures of 0, 12.5, 25, 27.5 and 50° and through the concentration range of 0.0005 to 0.01  $m$ . The theory based on the assumption of complete dissociation accounts quantitatively for the behavior of zinc sulfate up to a concentration of 0.01  $m$ , at which concentration the activity coefficient has fallen to a value of 0.38.

The value of the ion size parameter " $a$ " has been found to be constant from 0 to 37.5° and equal to 3.64 Å. This constancy of " $a$ " with temperature makes it probable that " $a$ " has the physical significance of the distance of closest approach of the unhydrated ions.

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