which was constructed from the vapor-pressure data, and should be used to extend the table of G., B. and S. below 30°K.

It may be noted that no work based on the temperature scale of G., B. and S. has yet been published, so that the adsorption error encountered will result in no corrections to the literature.

Summary

One of the standard copper-constantan thermocouples described by Giauque, Buffington and Schulze in the preceding paper has been compared with the oxygen and hydrogen vapor-pressure thermometers.

Complete agreement, within the limits of accuracy, has been found with the Leiden scale at the temperatures of liquid oxygen.

The hydrogen vapor-pressure measurements have shown that the scale of G., B. and S. is in error below 25°K., apparently due to adsorption of hydrogen in the gas thermometer.

A table showing the behavior of a typical copper-constantan thermocouple below 30°K. has been given to extend that of G., B. and S.

The triple-point pressure of hydrogen was found to be 5.370 international cm. of Hg. This value, when combined with the vapor-pressure results of Martinez and Onnes, gives a triple-point temperature of 13.92°K.

An equation for the vapor pressure of solid hydrogen is included.

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[CONTRIBUTION FROM GATES CHEMICAL LABORATORY, CALIFORNIA INSTITUTE OF TECHNOLOGY, NO. 141]

ACTIVITY COEFFICIENTS OF ELECTROLYTES. I
A BI-BIVALENT SALT AND THE ION ATTRACTION THEORY

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Introduction

The ion attraction theory developed first by Milner,[2] and more recently by Debye and Hückel,[3,4] has offered an apparently satisfactory explanation, at any rate at small concentrations, of the known behavior of strong electrolytes. The mathematical development of the theory shows why, and predicts how, the activity of an ion is related to the ionic strength. The equation for the activity coefficient γ of an ion with charge v as the ionic strength approaches zero is

$$\text{Log } \gamma = -Av^2 \sqrt{\tfrac{1}{2} \Sigma\, mv^2} \tag{1}$$

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[1] National Research Council Fellow in Chemistry.

[2] Milner, *Phil. Mag.*, **23**, 551 (1912); *ibid.*, **25**, 742 (1913).

[3] (a) Debye and Hückel, *Phys. Z.*, **24**, 185 (1923); (b) Debye, *ibid.*, **24**, 334 (1923).

[4] For a clear and critical presentation of this theory see A. A. Noyes, THIS JOURNAL, **46**, 1080 (1924).

In this expression A is composed of certain universal constants, the dielectric constant, D_0, of the solvent, and the absolute temperature. Using Drude's value, 78.77, for D_0 for water at 25°, the coefficient A becomes 0.505; using the recent value, 77.81, given by Kockel,[5] A becomes 0.514. La Mer, King and Mason[6] have obtained experimentally the value 0.528 for A from solubility measurements on the sparingly soluble tri-trivalent salt luteo-cobalt ferrocyanide and have calculated activity ratios for this salt which agree excellently with the theory.

In order to test the theory further with electrolytes of high-valence type, the activity coefficients of the bi-bivalent salt zinc sulfate were determined through electromotive-force measurements. Using the cell

$$\text{Zn-Hg (2 phase)} \mid ZnSO_4 \mid PbSO_4\ (s) + \text{Pb-Hg (2 phase)}$$

measurements were made over the concentration range from 0.0006 to 3.4 molal. 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 1 molal is related to the mean activity coefficient of the ions of the salt $\sqrt{\gamma\text{Zn}\ \gamma\text{SO}_4}$ and to its molality, m, as follows

$$E = E_0 - 0.059150 \log m \sqrt{\gamma\text{Zn}\ \gamma\text{SO}_4} \qquad (2)$$

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

$$E_0' = E + 0.059150 \log m \qquad (3)$$

Combined with (2) this gives

$$E_0' = E_0 - 0.059150 \log \sqrt{\gamma\text{Zn}\ \gamma\text{SO}_4} \qquad (4)$$

From Equation 1, using Kockel's value for D_0, we get for the bivalent salt

$$\log \sqrt{\gamma\text{Zn}\ \gamma\text{SO}_4} = -4.11 \sqrt{m} \qquad (5)$$

Combining this with (4), we obtain

$$E_0' = E_0 - 0.243 \sqrt{m} \qquad (6)$$

It is evident that a plot of E_0' against m should, as zero concentration is approached, give a straight line with slope —0.243, and that the correct extrapolation of the curve to zero will give E_0. Since the approach to linearity and the final slope constitute the test of the limiting equation, it was the author's purpose to determine this slope more accurately and with less uncertainty than has previously been possible from electromotive-force or freezing-point data.

Apparatus and Method

The Cell and Electrodes.—Although the attempts of some previous investigators[7,8] to use a lead-lead sulfate electrode were unsuccessful,

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[5] Kockel, *Ann. Physik*, [4] **77**, 417 (1925).

[6] La Mer, King and Mason, THIS JOURNAL, **49**, 363 (1927).

[7] Lewis and Brighton, *ibid.*, **39**, 1906 (1917).

[8] Horsch, *ibid.*, **41**, 1788 (1919).

Henderson and Stegeman[9] obtained very constant and reproducible results with the cell

Pb-Hg (2 phase) | $PbSO_4$ (*s*) | Na_2SO_4 (*s*) | Hg_2SO_4 (*s*) | Hg

A careful study of lead-lead sulfate electrodes was made by the present author, which led to the following conclusions: (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.

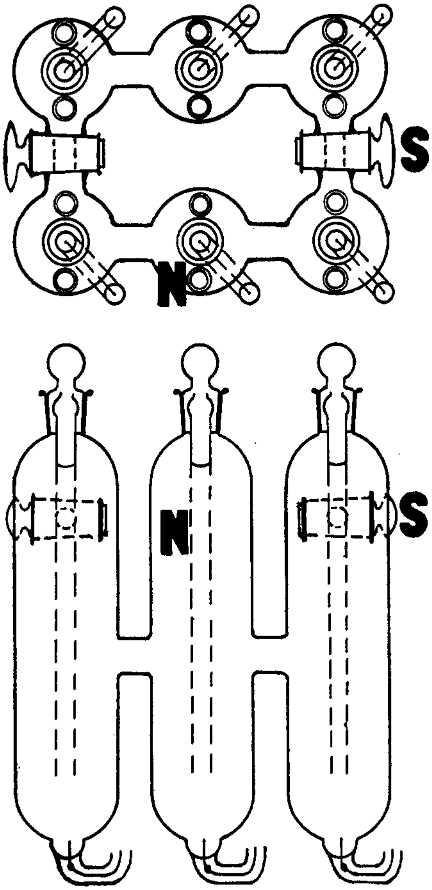

Fig. 1.

Fig. 1 shows diagrammatically the cell vessel used. The tubes marked N permitted nitrogen to be passed through the solution and were connected to glass manifolds by bits of rubber tubing carrying screw pinchcocks for equalizing the flow of gas in the different electrodes. A mercury trap on the outlet manifold prevented the diffusion of air into the cell when the flow of nitrogen was stopped. The passage of nitrogen through the cell served the double purpose of removing oxygen and of stirring the contents of the cell above the amalgams. The platinum wires sealed into the bottoms of the electrodes were fused to copper wires, eliminating the inconvenient use of mercury for electrical contacts to the measuring system. By using fairly small platinum wire, 0.4 mm. diameter, platinum-Pyrex seals may be made to hold satisfactorily. During the course of the experiments there has been no difficulty encountered from leakage through these seals.

Since the preparation of a satisfactory sulfate electrode for use in dilute solution requires attention to certain details, it seems desirable to describe the technique employed. The zinc sulfate solution to be used was first divided into two parts. To one part was added several grams of lead sulfate previously washed with the same solution, and the mixture

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[9] Henderson and Stegeman, This Journal, **40**, 84 (1918).

in a 1-liter, glass-stoppered, Jena glass bottle was rotated for 12–15 hours. At the end of this time, the electrode vessel, which had been dried at 115°, was filled with nitrogen by running a rapid stream of the gas through it for 5–10 minutes. The two-phase amalgams were heated until they became one-phase and were pipetted into the electrode vessel. Pyrex pipets of about 15 cc. capacity with an ungreased stopcock on the lower tube were used. A stream of nitrogen was passed through the cell while the amalgams cooled to room temperature. The half of the vessel containing the lead amalgam was filled with the solution saturated with lead sulfate after a layer of lead sulfate from the bottom of the flask had been pipetted onto the lead amalgam. The half containing the zinc amalgam was filled with the remainder of the solution which had not been saturated with lead sulfate. Large stopcocks and short tubes at S made it possible to make readings with the stopcocks closed in all but the two lowest concentrations. At these concentrations the initial level of liquid in the zinc side was made higher than in the lead side in order that when the stopcocks were opened for a reading the slight flow of solution would be from zinc to lead and never the reverse. After the cell had been placed in the thermostat, nitrogen was passed through for two hours. At the end of this time the cell had reached the temperature of the thermostat and its electromotive force was generally within less than a millivolt of the final constant reading.

The cell vessel (Fig. 1) is composed of six electrodes divided into two groups of three by the two stopcocks, S. On the one side, three similar lead sulfate electrodes were made and, on the other side, three zinc electrodes. The six external wires were connected to the potentiometer through a switchboard which permitted any pair of electrodes to be compared. The triplicate lead and triplicate zinc electrodes furnished a convenient and satisfactory check on the constancy and the reproducibility of the cell. In all of the experiments the zinc electrodes were found to check each other within 0.03 millivolt, and the sulfate electrodes to within 0.04 millivolt. Readings were taken on each cell over at least 36 hours after the cell had reached its final value (which was generally within six hours after the cell was made); and the degree of constancy obtained was such that the average reading of the combinations remained constant to within 0.04 millivolt over this period of time. In some of the experiments the cells were allowed to remain in the thermostat for a week before the divergence from the mean became as great as 0.2 millivolt.

In all solutions below 0.02 molal, another check on the cells was made by pipetting off the solution above the amalgams after the cell had been read for two days and introducing fresh solution. In four or five hours the cell would always come back to its previous reading.

Analysis of Zinc Solutions.—For experiments below 1 molal concentration two stock solutions of zinc sulfate were used. Into a weighed quantity of solution, a sufficient quantity of redistilled water was weighed. The stock solutions were analyzed by titrating potentiometrically with potassium ferrocyanide solution (twentieth molal, to each liter of which had been added 1 g. of potassium ferricyanide). A bright platinum wire and calomel electrode comprised the electrodes. A weighed sample of the solution was made acid with 5 cc. of 4 *N* sulfuric acid, diluted to 250 cc., heated to 70° and stirred while the titration was being made. With reasonable care this method of zinc analysis is good to 0.1%; often three or four check analyses will have a deviation of less than 0.05%. The potassium ferrocyanide solution was standardized, first, against Kahlbaum's "zur Analyse" zinc sticks scraped clean; second, by titrating the zinc sulfate residue left in a weighed platinum dish upon evaporation of a concentrated solution of zinc sulfate and heating the dish to 500°. The first method is the more exact but the second method was found to check to within 0.2%.

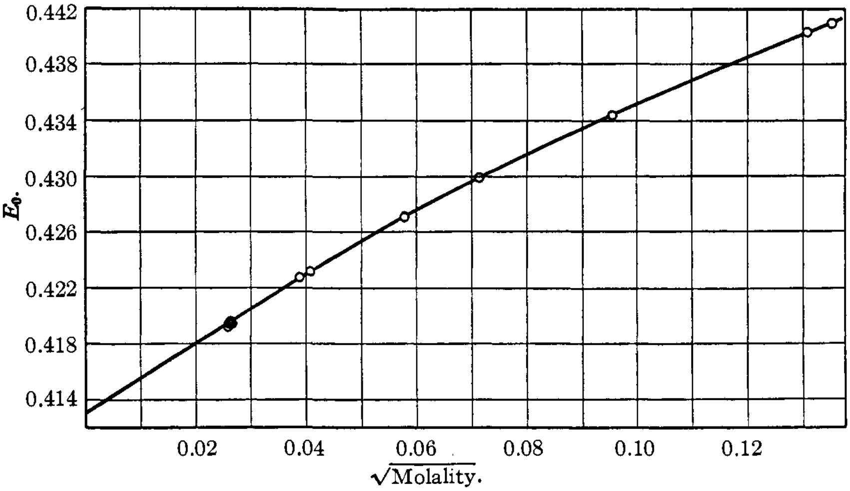

Fig. 2.—The zinc-lead cell at small concentrations.

The Measurements.—All measurements were made at 25.00 ± 0.01° in an oil-bath heated with a nichrome coil. The potentiometer was a Leeds and Northrup type K with Leeds and Northrup galvanometer No. 2500 B of resistance 460 ohms. The Weston standard cell used was checked at regular intervals against the laboratory standard cell.

Preparation of Materials

Lead Nitrate.—Merck's best grade of c. p. salt was recrystallized three times from hot water and the crystals were dried in air.

Lead Sulfate.—Since the lead sulfate was to be used in zinc sulfate solution, it was considered advisable to precipitate the lead sulfate with zinc sulfate. To a 5% solution of lead nitrate, made from the purified lead nitrate, was added an excess of a 10% solution of purified zinc sulfate. The liquid with its precipitate was heated to boiling and boiled for fifteen minutes, after which time the lead sulfate had assumed a definite, crystalline form. The lead sulfate was washed ten times by decantation and drained on a Buchner funnel. The material was then transferred to a wide-mouthed bottle and kept under distilled water until used. The author has found that in any case where a solid material is to be used for electrodes it is advisable to keep the material under water until it is used.

Zinc Sulfate.—The best grade of $ZnSO_4.7H_2O$ was recrystallized three times from hot water. According to Mellor[10] the maximum solubility of zinc sulfate is at 70°. The heptahydrate obtained on slowly cooling the solution was partially dried in air.

Lead Amalgam.—Into mercury which had been carefully purified[11] lead was electrolyzed from a solution of lead nitrate. The anode consisted of platinum foil placed in another beaker filled with 1 N HNO_3, and connected to the first beaker by means of a Y-tube. A paddle stirrer was placed in the mercury in the cathode beaker so as to slowly stir the mercury during the electrolysis. The current was 0.1 ampere and was run until the concentration of lead in the amalgam was about 3%. The amalgam was washed, dried and heated until it became one-phase and filtered through a capillary tube into an evacuated flask which was then filled with nitrogen.

Zinc Amalgam.—Sticks of Kahlbaum's "zur Analyse" grade of zinc were purified by rapid electrolysis with 3–4 amperes. The zinc crystals were washed, drained and weighed moist. A weighed quantity of mercury corresponding to 3% zinc was added to the moist crystals; the mass was then covered with a dilute solution of nitric acid and stirred until all the zinc crystals had gone into the amalgam. After washing, drying, heating and filtering through a capillary tube into a vacuum the amalgam was stored under nitrogen in the same way as the lead.

Nitrogen.—Tank nitrogen was purified by the van Brunt method.[12] The gas after leaving the dilute sulfuric acid wash bottle was dried by passing through a tower filled with soda lime. Passing through a three-way stopcock, the gas was used dry or led into a bubbler filled with a zinc sulfate solution of the concentration used in the cell and thence into the cell vessel.

The Experimental Data

In Table I are given the experimental data and the calculated function E_0'. The observed electromotive forces given in Col. 2 are in every case the average of the combination of the six electrodes described above.[13]

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[10] Mellor, "Inorganic and Theoretical Chemistry," Longmans and Co., London, **1923**, Vol. IV, p. 614.

[11] Fay and North, *Am. Chem. J.*, **25**, 216 (1901).

[12] Van Brunt, THIS JOURNAL, **36**, 1448 (1914).

[13] A correction for the solubility of lead sulfate was made at the concentrations of 0.003 M and less. This was done by calculating the increase in sulfate-ion concentration in the solution coming from the solubility of lead sulfate, and by obtaining the corresponding potential resulting therefrom by means of the usual equation $E = 0.0296 \log c_1/c_2$. Böttger (*Z. phys. Chem.*, **46**, 604 (1903)) found the solubility of lead sulfate at 25° to be 1.34×10^{-4} M. From the limiting ion attraction equation, γ is found to be 0.88 at this concentration, so that the solubility product of lead sulfate is 1.39×10^{-8}. From the quadratic equation $(\gamma m + x)x = 1.39 \times 10^{-8}$, by substituting the values of γ calculated from the limiting equation, the value of the increase x in the sulfate-ion concentration due to the lead sulfate was obtained and, by completing the calculations indicated above, we get the following corrections which have been added to the observed voltages: 0.0033 M, 0.00004 v.; 0.0016 M, 0.00012 v.; 0.0015 M, 0.00013 v.; 0.00069 M, 0.00055 v.; 0.00067 M, 0.00058 v.; 0.00066 M, 0.00059 v.

TABLE I

THE OBSERVED ELECTROMOTIVE FORCES OF THE ZINC-LEAD CELL AT 25°C.

Molality, M per 1000 g. of H_2O	Electromotive force E	E'_0
0.0006580	0.60744	0.41924
.0006699	.60723	.41949
.0006866	.60671	.41960
.0007016	.60603	.41949
.001505	.58978	.42283
.001648	.58783	.42321
.003322	.57374	.42713
.005064	.56576	.42996
.009096	.55520	.43447
.01712	.54490	.44041
.01824	.54391	.44105
.04120	.53175	.44982
.08532	.52114	.45801
.1732	.51219	.46715
.2532	.50766	.47237
.3518	.50366	.47682
.8564	.49320	.48922
1.426	.48585	.49497
2.052	.47827	.49674
2.749	.46855	.49453
3.419	.45811	.48969

TABLE II

THE MEAN ACTIVITY COEFFICIENTS OF ZINC SULFATE AT 25°

Molality, M	E.m.f., E'_0	Mean activity coefficients of Zn^{++} and SO_4^{--} From e.m.f.	From ion attraction theory	Percentage difference
0.0001	0.41553	0.907	0.910	+0.3
.0005	.41866	.803	.809	+ .7
.001	.42097	.734	.741	+1.0
.002	.42410	.650	.654	+0.6
.005	.42985	.519	.512	−1.3
.01	.43528	.421	.388	−7.8
.02	.44196	.324	.262	−19.1
.05	.45190	.220	.120	−45.4
.08	.45762	.176		
.1	.45991	.161		
.2	.46905	.113		
.3	.47460	.0910		
.5	.48172	.0690		
.8	.48830	.0534		
1.0	.49120	.0477		
1.5	.49538	.0405		
2.0	.49670	.0385		
2.5	.49569	.0400		
3.0	.49295	.0445		
3.5	.48907	.0518		

As a final check on the measurements in the very dilute solutions, a flowing electrode using a dilute (0.03%) zinc amalgam was employed in the zinc half-cell for the concentrations 0.001505 M and 0.0007016 M. The potential of this dilute amalgam electrode against the two-phase zinc amalgam electrode was found to be 0.04750 volt. The voltages given in the table for the two cells referred to are corrected for this difference.

From a large-scale plot of E_0' against $\sqrt{m}$, values of E_0' at round concentrations were read, and the corresponding mean activity coefficients were calculated by Equation 4, using the value of E_0 determined by the extrapolation described below. These values are given in Table II along with the coefficients calculated from the ion-attraction theory, using Kockel's value for $A = 0.514$ up to where the percentage deviation from the limiting equation becomes enormous.

Discussion of the Results

The experimental values of E_0' fall so well upon a smooth curve which rapidly approaches linearity below 0.01 M that the final slope can be determined with almost no ambiguity by plotting the slope of the curve at even intervals against the corresponding value of $\sqrt{m}$ and obtaining the constant value approached in the most dilute solutions. This final slope is found to be —0.248, which corresponds to 0.523 for the value of A in Equation 1.

Extrapolating the $E_0'/\sqrt{m}$ curve to zero concentration asymptotic to a straight line with this slope of —0.248, the electromotive force of the cell when the zinc ions and sulfate ions have activities of 1 molal is found to be 0.41302 volt.

The validity of the ion attraction theory at small concentrations is also made evident by the agreement of the experimental and theoretical activity coefficients given in Table II. Up to 0.005 molal (an ionic strength of 0.02) the agreement is within 2%, and perhaps within the experimental error. This is a very striking fact when it is considered that at 0.005 molal the activity coefficient has already fallen to nearly 0.5.

A scarcely less striking fact is the rapidity with which, as the molality further increases, the actual activity coefficients deviate from those calculated by the limiting equation of the ion attraction theory. Thus, at 0.02 molal the deviation is already 19.1% and at 0.05 molal it is 45.4%. These results illustrate the great error that is made in applying mass-action equations that assume complete ionization and ion activities calculated even by the Debye-Hückel equation to equilibria involving bivalent ions at normalities greater than 0.01 normal. They also show that the theoretical corrections that must be introduced into the limiting equation of the ion attraction theory to make it apply at even moderate concentrations must be such as will account for the very large deviations in the case of ions of higher valence.

That these corrections cannot consist merely in taking into account the size a of the ion by introducing a factor $(1 + Ba\sqrt{\Sigma\ mv^2})$ is indicated by the slow increase of this function with the ionic strength. It has indeed been shown by La Mer[6] and his co-workers and by Schärer[14] that the observed solubility effects cannot be accounted for in this way.

The author wishes to express his appreciation to Professor A. A. Noyes for his interest and helpful suggestions in carrying out this research.

Summary

The preparation of a reproducible lead-lead sulfate electrode has been described. Electromotive-force measurements at 25° on the cell Zn-Hg (2-phase) | $ZnSO_4$ | $PbSO_4$ (*s*) | Pb-Hg (2-phase) have been given over the concentration range 0.0006 to 3.4 molal. The potential of the cell when the ion activities are 1 molal has been found to be 0.41302 volt.

The mean ion activity coefficients for zinc sulfate through this concentration range have been calculated. The rapid decrease of these activity coefficients with increasing concentration is striking. Thus, the value has become 0.42 at 0.01 molal and 0.16 at 0.1 molal.

The experimental results at small concentrations are found to be in good agreement with the limiting equation of the ion-attraction theory. Thus the experimentally found value for the constant in the equation is 0.523, while the calculated value is 0.504 or 0.514, depending on whether Drude's or Kockel's value for the dielectric constant of water is used.

At molalities above 0.005 the deviations between the theoretical and observed values increase with extraordinary rapidity, showing that in the case of ions of higher valence the theoretical equation must have very substantial corrections applied to it, besides that of taking into account the size of the ions.

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[14] Schärer, *Physik. Z.*, **25**, 145 (1924).