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THE ACTIVITY COEFFICIENTS AND HEATS OF TRANSFER OF CADMIUM SULFATE FROM ELECTROMOTIVE FORCE MEASUREMENTS AT 25 AND 0°. APPLICATION OF THE EXTENDED THEORY OF DEBYE AND HÜCKEL

BY VICTOR K. LA MER AND W. GEORGE PARKS¹

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Introduction

The activity coefficients of many typical electrolytes have been determined in both dilute and concentrated solutions, but few results have been reported for cadmium sulfate. The only available data are found in the work of Getman² on the electromotive force of galvanic cells and in the table of activity coefficients compiled by Lewis and Randall.³ The latter results were calculated from the freezing point data collected in the paper of Lewis and Linhart.⁴ The results of Getman are not consistent, while those tabulated by Lewis and Randall do not extend below a concentration of 0.01 molal.

Since it is well known that the halides of cadmium are somewhat anomalous in their behavior as electrolytes, this research was undertaken to establish the activity of the sulfate over the entire concentration range by measuring the electromotive force of the cell



and to obtain data on an electrolyte of the symmetrical (2-2) valence type, which are well suited for testing the mathematical extension of the Debye-Hückel theory given by Gronwall, La Mer and Sandved.⁵

The previous electromotive force studies on cadmium sulfate have always involved the mercurous sulfate half-cell, but since lead sulfate is about one-tenth as soluble as mercurous sulfate, it is obvious that precise measurements can be extended to much lower concentration with the lead sulfate-lead half-cell.

If the temperature coefficient of such a cell is also measured, it becomes possible to determine not only the change in heat content of the reaction through the Gibbs-Helmholtz equation, but also to evaluate the electrical heat of transfer arising from electrostatic interaction by taking advantage of the accurate extrapolation afforded by the extension of the Debye-

¹ This paper is constructed from a dissertation submitted by W. George Parks in partial fulfillment of the requirements for the degree of Doctor of Philosophy in the Faculty of Pure Science, Columbia University, 1930.

² Getman, *J. Phys. Chem.*, **32**, 91 (1928).

³ Lewis and Randall, "Thermodynamics and the Free Energy of Chemical Substances," McGraw-Hill Book Co., Inc., New York, 1923, p. 362.

⁴ Lewis and Linhart, *THIS JOURNAL*, **41**, 1951 (1919).

⁵ Gronwall, La Mer and Sandved, *Physik. Z.*, **29**, 358 (1928), see p. 388, eq. 107.

Hückel theory given by Gronwall, La Mer and Sandved. Although free energy measurements at two temperatures alone afford only a partial answer to the question of electrical heats of dilution, they are sufficient to determine the temperature coefficient of the parameter " a " representing the distance of closest approach of the ions. The value of $\partial "a" / \partial T$ is of considerable theoretical interest in considering heats of dilution.

Theoretical

Although there have been many experimental investigations which have demonstrated that the activity coefficients of strong electrolytes in aqueous solution agree with the predictions given by the equations of Debye and Hückel sufficiently well to establish inter-ionic attraction as the explanation of the anomalies of strong electrolytes, nevertheless, it is true that experimental data exist which exhibit serious discrepancies from these equations in regions of high dilution. These discrepancies are quite unexpected on the basis of the Debye-Hückel equations. They appear most conspicuously in the case of high valence types in water as well as for univalent types in media of lower dielectric constant. On the other hand, data on higher valence types furnish the most convincing tests of the theory since the deviations measured are more significant and not subject to the same degree of experimental uncertainty that accompanies the data for lower valence types.

In this Laboratory we have held that the incomplete mathematical solution for the Poisson-Boltzmann equation as given by Debye and Hückel should first be completed and the data tested from that viewpoint, before ascribing the discrepancies between the abridged theory and experiment to new physical hypotheses such as incomplete dissociation, deformability of the ions, or even the ion-association hypothesis of Bjerrum.⁶ This procedure has the advantage that the theory is not weakened by the immediate introduction of further arbitrary parameters which accompany new physical assumptions. Evidence that a more complete mathematical treatment without further assumptions is sufficient to account for data which are in apparent disagreement with the theory should furnish one of the most satisfying experimental proofs possible.

Whenever it is found that the general solution of the Poisson-Boltzmann equation is incapable of describing the behavior quantitatively on the basis of a constant and physically reasonable value of " a ," it then becomes appropriate to ascribe such discrepancies to incomplete dissociation as embodied in the term "weak salt."⁷

⁶ Bjerrum, *Det. Kgl. Danske Videnskab. Math.-fys. Medd.*, VII, No. 9 (1926). Bjerrum's ion-association introduces no new parameter but necessitates an arbitrary distinction between free and associated ions which becomes superfluous in the extension of Gronwall, La Mer and Sandved.

⁷ Randall and Scott, *THIS JOURNAL*, 49, 647 (1927); Randall and Allen, *ibid.*, 52, 1814 (1930).

Since the extended theory of Debye and Hückel makes no pretense of dealing with factors other than electrostatic interaction it is important to ascertain to what concentration limit it is competent to account for the facts under the present incorrect but necessary approximation that the dielectric constant of the solution D is equal to the dielectric constant of the pure solvent D_0 .

We shall be primarily concerned with the error introduced by Debye and Hückel in retaining only the linear term of the expansion of the expression for the density of electricity ρ valid for a symmetrical electrolyte like cadmium sulfate where $z_1 = -z_2 = z = 2$

$$\rho = nze \left(e^{-ze\psi/kT} - e^{ze\psi/kT} \right) \cong -2ne^2z^2\psi/kT \quad (2)$$

when this approximation for ρ is introduced into the Poisson equation

$$\nabla^2\psi = \frac{-4\pi\rho}{D} \cong \kappa^2\psi \quad (3)$$

where

$$\kappa = \sqrt{\frac{8\pi ne^2z^2}{DkT}} \quad (4)$$

The complete solution⁵ of (2) and (3) for the activity coefficient of a salt of the symmetrical type takes the form

$$\log f = \frac{-\epsilon^2z^2}{kTDa} \cdot \frac{1}{2} \cdot \frac{x}{1+x} + \sum_{m=1}^{\infty} \left(\frac{\epsilon^2z^2}{kTDa} \right)^{2m+1} \left[\frac{1}{2} X_{2m+1}(x) - 2m Y_{2m+1}(x) \right] \quad (5)$$

where $x = "a"\kappa$ and $X(x)$ and $Y(x)$ are functions of x defined and tabulated through the fifth approximation,⁵ *i. e.*, $m = 2$. Employing Drude's value of $D = 78.77$ for 25° , $\kappa = 0.3283 z \sqrt{M}$, we get the working equation suitable for numerical calculation

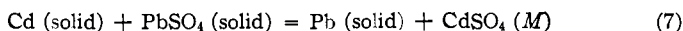
$$\begin{aligned} -\log_{10} f = 1.53636 \left(\frac{z^2}{a} \right) \frac{x}{1+x} &- 0.15382 \left(\frac{z^2}{a} \right)^3 \cdot 10^8 \left[\frac{1}{2} X_3(x) - 2Y_3(x) \right] \\ &- 0.0770 \left(\frac{z^2}{a} \right)^5 \cdot 10^8 \left[\frac{1}{2} X_5(x) - 4Y_5(x) \right] \quad (6) \end{aligned}$$

A rough computation will show that whenever a/z^2 is assigned values $> 1.5 \text{ \AA.}$, only the first term corresponding to the Debye-Hückel approximation need be considered in most work. However, when $a/z^2 < 1.5 \text{ \AA.}$, which means $"a" < 6 \text{ \AA.}$ for a bi-bivalent salt, the contribution of the higher terms cannot be neglected. They will be important for (2-2) salts since 6 \AA. is a large ion size. In low dielectric solvents the higher terms become important, in fact, may occasionally predominate over the first approximation even for (1-1) valence types, since the significant parameter is Da/z^2 .

In the first approximation as given by Debye and Hückel the limiting law is the asymptote when *either* $"a"$ or the concentration factor $\kappa = 0.3283 z \sqrt{M}$ is assigned values approaching zero, whereas in the general development of Gronwall, La Mer and Sandved, the limiting law is the asymptotic form *only* when κ approaches zero. In the general solution the correction terms assume infinite values *whenever* $"a" \rightarrow 0$. The

correctness⁸ of this latter statement will be immediately evident when one recognizes that the field strength at the surface of a point charge is infinite. An assembly of point charges would condense together and it would require an infinite amount of work to separate such hypothetical ions. In other words, the logarithm of the activity coefficient would be infinite when "a" is set equal to zero. The indiscriminate use of the Debye-Hückel approximation may therefore easily yield absurd values for "a" when their equations are employed in the computation of experimental data on higher valence electrolytes. The general solution⁵ overcomes this mathematical difficulty and should yield positive and physically reasonable values for "a" which are constant over a legitimate concentration range, provided the theory is correct in its fundamental postulates. It is our purpose to test this point.

The electromotive force of the cell (1) corresponding to the process



is given by the equation valid for 25°

$$E = E_0 - 0.05915 \log m - 0.05915 \log f \text{ (volts)} \quad (8)$$

For convenience in plotting and calculating the activity coefficient $f_{\text{CdSO}_4} = \sqrt{f_{\text{Cd}^{++}} \cdot f_{\text{SO}_4^{--}}}$, we calculate the quantity E'_0 , where

$$E'_0 = E + 0.05915 \log M, \text{ and} \quad (9)$$

$$E'_0 = E_0 - 0.05915 \log f \quad (10)$$

If we use the Debye-Hückel limiting law valid for a bi-bivalent salt, namely

$$\log f = -4.04 \sqrt{M} \quad (11)$$

we get

$$E'_0 = E_0 - 0.239 \sqrt{M} \quad (12)$$

It is evident that a plot of E'_0 against \sqrt{M} should approach a limiting tangent with slope 0.239, the intercept being E_0 . Although this method of extrapolating for E_0 is widely used, it is open to the objection that it places the most weight upon the points in dilute solution, which are the most difficult to determine with accuracy. Furthermore, it assumes that the Debye-Hückel limiting law is obeyed exactly throughout the region of extrapolation.

A consideration of the magnitude of the third and fifth approximations ($m = 1$ and 2) in equation (5) shows that this assumption is not justified for any physically attainable concentration for a (2-2) salt. In fact, it cannot be emphasized too strongly that the *percentage error* in $\log f$ due to the neglect of the higher terms is most significant in the region of highly dilute solutions, *i. e.*, from about 0.0001 to 0.001 molal. The first approximation as given by Debye and Hückel predicts just the opposite.

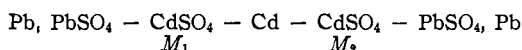
⁸ La Mer, *Trans. Am. Electrochem. Soc.*, 61, 543 (1927). A mathematical proof is given in Ref. 5, Chapt. 2, p. 360.

We therefore employ the method of assuming an "a" value and calculate the value of E_0 through equations (6) and (10). That value of "a" which gives a constant E_0 value over the range of concentration for which it is legitimate to employ equation (6) under the assumption $D = D_0$ is taken as the true value. This method assigns equal weight to all the experimental points, and is not open to personal interpretation as is a graphical extrapolation.

From the data it is possible to compute the free energy of transfer accompanying changes in concentration of the solution. The free energy change $\Delta F = \Delta \bar{F}_{\text{CdSO}_4}$ involved in transferring a mole of salt from a molality M_1 to a molality M_2 is given by the formula

$$-\Delta F = \frac{2 \times \Delta E \times 96,500}{4.182} \text{ calories} \quad (13)$$

where ΔE is the electromotive force of the cell



corresponding to the process $\text{CdSO}_4 (M_1) \longrightarrow \text{CdSO}_4 (M_2)$.

The thermal change accompanying a chemical reaction can be calculated readily from the temperature coefficient of the electromotive force of a cell in which the particular reaction takes place. Thus, on substituting in the Gibbs-Helmholtz equation

$$-\Delta H = nF \left(E - T \frac{\partial E}{\partial T} \right) \quad (14)$$

the observed value of E , at the temperature T , and the value of $(\partial E/\partial T)$ derived from the observed variation of E with T , we calculate the value of ΔH at the temperature T and molality M , where the solid cadmium and lead are saturated with mercury.

Owing to experimental difficulties which will be discussed later, sufficient data have not as yet been obtained for an exact calculation of the heat of the reaction. However, as a first approximation we may assume that $(\Delta E/\Delta T)_M = (\partial E/\partial T)_M$ and complete the calculation indicated by Equation 14, taking E for 12.5° as the mean of E_{25° and E_{0° .

Preparation of Materials

Lead Nitrate.—The best grade of c. p. salt was recrystallized three times from boiling distilled water and the crystals were dried in air.

Cadmium Sulfate.—Since cadmium sulfate has a negative temperature coefficient of solubility, forming solid hydrates at low temperatures, the best grade of salt was recrystallized three times from boiling distilled water by slowly evaporating the solution to about one-third of its original volume. The crystals were then powdered in an agate mortar and heated in a large quartz dish to about 250° for six hours, forming anhydrous cadmium sulfate. According to Mellor,⁹ when cadmium sulfate is recrystallized from water above 74° the product obtained is $\text{CdSO}_4 \cdot \text{H}_2\text{O}$. This monohydrate Mylius and

⁹ Mellor, "Treatise on Inorganic and Theoretical Chemistry," Vol. IV, p. 615.

Funk¹⁰ found decomposed into the anhydrous salt at 112°. Coniglio¹¹ reports for this transition temperature 150 to 170°. Partridge¹² in preparing his highly purified cadmium sulfate heated it to 200° for six hours. The prepared salt was preserved until used in a weighing bottle over phosphorus pentoxide.

Lead Sulfate.—The lead sulfate was precipitated from a cadmium sulfate solution by adding a 5% solution of the purified lead nitrate to an excess of a 10% solution of the purified cadmium sulfate. The solution containing the precipitate was heated to boiling for fifteen minutes, at the end of which time the lead sulfate had assumed a definite crystalline form. It was washed with distilled water, drained on a Büchner funnel, and preserved under distilled water in a Non-Sol bottle until needed in the electrodes.

Mercury.—Redistilled mercury was stirred under dilute nitric acid for twenty-four hours and then twice redistilled by the Hulett¹³ method in a slow current of air.

Lead Amalgam.—Lead amalgam was prepared by electrolyzing the purified lead nitrate solution using purified mercury as the cathode. The anode consisted of a platinum wire placed in another beaker filled with 1 *N* nitric acid, and connected to the first beaker by means of a Y-tube. This was necessary because lead peroxide forms at the anode during electrolysis. A paddle stirrer was placed in the cathode beaker to slowly stir the mercury. A current of 0.2 ampere was run until the concentration of lead in the amalgam was about 6%. Fay and North¹⁴ report that all amalgams between the limits of 2 and 55% of lead form a two-phase system at 25°, consisting of a granular phase of constant composition represented by Pb₂Hg, and a liquid phase which also has a definite composition when equilibrium is reached. Puschin¹⁵ found that all amalgams between 1.8 and 66% lead have the same electromotive force. Likewise Henderson and Stegeman¹⁶ report that in their work they found the same value for the electromotive force of any amalgam containing between 2.5 and 6% lead.

The prepared amalgam was washed, dried, heated until it became one phase and filtered through a capillary tube into the evacuated reservoir, which was then filled with purified nitrogen and stored ready for use.

Cadmium Amalgam.—Using a mercury cathode, as in the case of the lead amalgam, cadmium was electrolyzed from a solution of purified cadmium sulfate. The anode consisted of a bar of C. P. cadmium, scraped clean of oxide. A current of 0.2 ampere was employed until the concentration of cadmium in the amalgam was about 11%. Frilley¹⁷ reports that all amalgams of less than 5% are liquid. The solubility of cadmium in mercury was found by Hulett and deLury¹⁸ to be 5.574 g. per 100 g. of mercury at 25°. Bijl¹⁹ shows that all amalgams between 5 and 14% of cadmium have the same electromotive force when measured against any constant electrode at room temperature. The solid phase in the amalgam is reported by Kerp and Böttger²⁰ to have the composition represented by Cd₂Hg. However, they admit that there is some evidence that the solid phase may be a mixed crystal.

This amalgam was washed, dried, heated and stored under nitrogen in the same way

¹⁰ Mylius and Funk, *Ber.*, **30**, 825 (1897).

¹¹ Coniglio, *Rend. accad. Sci.*, (Napoli), [3] **34**, 119 (1928).

¹² Partridge, *Am. J. Sci.*, [3] **40**, 381 (1890).

¹³ Hulett, *Phys. Rev.*, **21**, 288 (1905); *ibid.*, **33**, 307 (1911).

¹⁴ Fay and North, *Am. Chem. J.*, **25**, 216 (1901).

¹⁵ Puschin, *Z. anorg. Chem.*, **36**, 210 (1903).

¹⁶ Henderson and Stegeman, *THIS JOURNAL*, **40**, 84 (1918).

¹⁷ Frilley, *Rev. métal.*, **8**, 541 (1911).

¹⁸ Hulett and deLury, *THIS JOURNAL*, **30**, 1811 (1908).

¹⁹ Bijl, *Z. physik. Chem.*, **41**, 641 (1902).

²⁰ Kerp and Böttger, *Z. anorg. Chem.*, **25**, 54 (1900).

as the lead. In the preparation of both amalgams the concentration of electrolyte was kept high and the potential drop between the electrodes low so that the deposition of possible impurities was negligible. A concentration of metal in the amalgams was used such that the temperature could be varied from 0 to 50° and a two-phase system would result when equilibrium was attained.

Nitrogen.—Tank nitrogen was purified by passing it first through potassium pyro-gallate, freshly prepared according to the method of Berthelot,²¹ and then over-heated copper gauze in a quartz tube. The gas passed through a gas washing bottle filled with dilute sulfuric acid, followed by a tower filled with soda lime. Before entering the cell vessel the gas bubbled through a long upright tube filled with some of the solution in the cell to ensure the same aqueous tension.

Experimental Method

Cell and Electrodes.—Although the attempts of some previous investigators²² to use the lead-lead sulfate electrode were unsuccessful, Henderson and Stegeman¹⁶ obtained constant and reproducible results with the electrode in the presence of sodium sulfate. U. B. Bray²³ made a careful study of the electrode in the presence of zinc sulfate. He found that: (1) oxygen must be excluded. (2) A definite crystalline form of lead sulfate is essential. (3) It is best to establish equilibrium between

the solid lead sulfate and the solution before the electrode is made up. (4) The use of two-phase amalgams is highly desirable, making the electrode easily reproducible without analysis. We confirm Bray's findings that the lead sulfate electrode is highly reproducible if these conditions are observed, but since his experimental details are scanty and we also had initial difficulties we give our procedure in some detail.

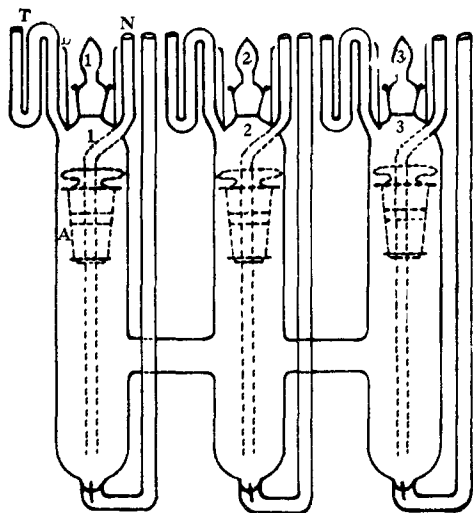


Fig. 1.

three similar lead electrodes, on the other side three similar cadmium electrodes were set up. These served as a convenient and satisfactory means of checking the constancy and reproducibility of each half-cell. Through the tubes marked N nitrogen could be

²¹ White, "Gas and Fuel Analysis," McGraw-Hill Book Co., Inc. New York, 1920, p. 33.

²² Lewis and Brighton, *THIS JOURNAL*, 39, 1906 (1917); Horsch, *ibid.*, 41, 1788 (1919).

²³ U. B. Bray, *ibid.*, 49, 2372 (1927).

passed through the solutions to remove oxygen and facilitate equilibrium by stirring. These tubes were connected to a glass manifold made of Pyrex tubing carrying capillary tubing outlets for equalizing the flow of gas. The connections to the cell vessel were made with small bits of rubber tubing carrying pinch clamps to further regulate the flow when necessary. All rubber tubing was painted with castor oil and shellac. Small glass traps, marked T, were sealed on each electrode so that when the flow of nitrogen was stopped a few drops of mercury in each trap would prevent the diffusion of air into the cell. The lines on Fig. 1 marked B designate short pieces of large glass tubing sealed on each electrode with "picein" cement so that a mercury seal could be made over each ground glass joint. Later this method was discarded, the tubes were removed, and a few drops of castor oil placed in the gutter of each ground joint, a method which proved entirely satisfactory.

The technique for filling the cell was as follows. The cadmium sulfate solution to be used was divided into two parts. To one part was added several grams of solid lead

sulfate which had previously been washed with the cadmium sulfate solution, and the mixture rotated for fourteen hours in the thermostat. After carefully cleaning and drying the electrode vessel it was filled with nitrogen. One side of the cell was then filled with the cadmium sulfate solution saturated with lead sulfate and the other side with the pure cadmium sulfate solution. The cell was put in the thermostat and nitrogen bubbled through for one hour. At the end of this time the amalgams were added from the reservoirs in which they were stored. A sketch of one of these reservoirs is given in Fig. 3. Boiling water was poured into the outside jacket marked A in order to heat the amalgam until it became one phase. Then after a few drops had been run out at the stopcock B to remove any amalgam that may have been in the tube in contact with the air, the electrode vessel was placed under the reservoir and the required amount of amalgam dropped through a very small funnel into the proper cell. Any oxide which is formed in the preparation of the amalgams is almost entirely removed on filling the reservoirs through the fine capillary tube C (Fig. 3). The possibility of contamination from the traces of oxide remaining on the surface of the amalgams in the reservoirs is eliminated by filling each electrode with amalgam drawn from the bottom (stopcock B) and by passing the amalgam through the small funnel holding a filter paper with a pin hole opening. The cell was replaced in the thermostat, nitrogen continued for two hours more and the apparatus then

sealed. Gas was passing through each electrode while the amalgams were being added. Large stopcocks (5 mm. bore) and short tubes at A (Fig. 2) made it possible to measure the electromotive force with the stopcocks closed in all cases except for the solutions of about 0.002 molal and less. For these solutions, the hole in each stopcock held a plug of cotton previously soaked in the cadmium sulfate solution being used; also the level of the solution on the side containing no lead sulfate was made higher so that when the

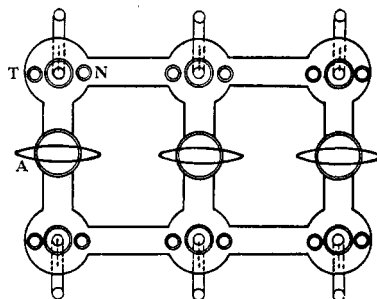


Fig. 2.

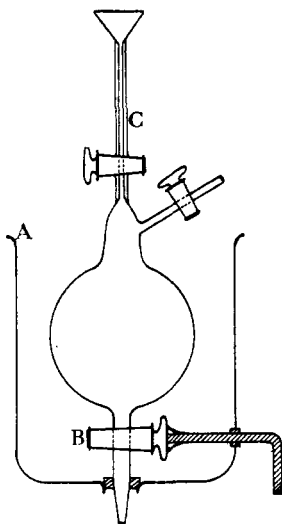


Fig. 3.

stopcocks were temporarily opened for making a reading no lead sulfate could possibly siphon over to the cadmium side. A slight movement of the solution in the other direction is of no consequence, since it soon becomes saturated with lead sulfate.

The reproducibility of the cadmium electrodes was usually to within 0.01 millivolt. In the more dilute solutions a check of 0.06 millivolt was considered satisfactory for the lead electrodes. In the more concentrated solutions the agreement was much better. Frequently, as with the cadmium electrodes, no difference greater than ± 0.01 millivolt was observed. Readings were taken for at least twenty-four hours after the cells had reached their final constant value, which was usually about six hours after preparation. In the concentrated solutions, 1 molal and greater, this time of equilibrium was extended over forty-eight to seventy-two hours. The average reading of the nine combinations remained constant to 0.04–0.05 millivolt for from thirty-six to forty-eight hours after the equilibrium value was reached. In nearly all of the solutions below 0.008 molal check determinations were made. The values for the lowest three concentrations reported were not as reproducible as desired and will be discussed in more detail later.

When attempts were made to measure the electromotive force at 37.5 and 50° the agreement was never better than one to two millivolts, so no results are recorded for these temperatures. This failure at the higher temperatures is attributed to the transition of α -cadmium to β -cadmium. Getman²⁴ reports that α -cadmium is the stable form at ordinary temperatures and that this form changes to β -cadmium at 37 to 40° depending upon the thermal history of the metal employed, whereas Cohen and Helderman²⁵ give the transition point in the vicinity of 64°.

In making the measurements at the different temperatures, the cell vessel, after the electromotive force had been measured at 25°, was treated in the following manner. In order to prevent the change in pressure from drawing the mercury from the traps into the cell or forcing out of any of the cell contents, small corks were forced into the traps on top of the mercury and capped by a few drops of castor oil. The glass stopcock on the nitrogen inlet manifold was closed. The slight change in pressure in the system due to changing temperature was too small to produce a measurable change in volume of the liquid and solid reactants.

The equilibrium value at 0° was usually reached in from twelve to sixteen hours. No measurements were attempted below a concentration of 0.0007 molal at 0° because the internal resistance of the cell was then too great. A variation of from 0.05 to 0.1 millivolt in the most dilute solutions was considered satisfactory at this temperature.

Preparation and Analysis of Cadmium Solutions.—For all concentrations above 0.1 molal the solutions were made up by direct weighing of the salt and water. For the concentrations below 0.1 molal stock solutions of cadmium sulfate were diluted by weight. The distilled water averaged 1.2×10^{-6} reciprocal ohms for the specific conductivity; occasionally water with a specific conductivity of 0.7×10^{-6} r. o. was obtained.

The stock solutions were analyzed electrolytically by depositing the cadmium on a platinum gauze electrode from a cyanide bath. A weighed sample of the solution to be analyzed was made decidedly alkaline with potassium hydroxide and then just enough potassium cyanide added to dissolve the precipitate. A current of 0.5 ampere was passed through the solution for twenty-four hours using a platinum wire anode and a platinum gauze cathode of 30 sq. cm. in area. The solution was slowly stirred all the time. At the end of this time not the faintest trace of color could be obtained by passing hydrogen sulfide into the solution. The cathode was then washed with alcohol and ether.

²⁴ Getman, *THIS JOURNAL*, 39, 1806 (1917).

²⁵ E. Cohen, "Physico-Chemical Metamorphosis and Problems in Piezochemistry," McGraw-Hill Book Co., Inc., New York, 1928, pp. 40–50.

dried and weighed. It was possible to obtain triplicate determinations which agreed to within 0.1%. On several occasions the results checked to 0.05%. Using this method of analysis the average cadmium content of the purified anhydrous cadmium sulfate agreed within one part in 20,000 of the theoretical value.

Other methods of analysis were tried, including the precipitation of cadmium as cadmium sulfide and the precipitation of sulfate as barium sulfate. These methods were not as reproducible as the electrolytic method nor did they check well with one another.

The Apparatus.—For measurements at 25° a large water thermostat was maintained to $\pm 0.01^\circ$. The Beckmann thermometer was checked against the laboratory standard, and also against a thermometer calibrated by the Bureau of Standards. For the measurements at 0° a small bath of ice and water mush was used, having air lift pumps to provide adequate circulation. This bath was maintained to $\pm 0.05^\circ$. The potentiometer was a Leeds and Northrup type K, with a high resistance galvanometer No. 2500 type R, having a sensitivity of 424 megohms, a period of 2.8 seconds, and an external critical damping resistance of 2000 ohms. The potentiometer was calibrated, and the Weston standard cell was certified by the Bureau of Standards. The standard cell was kept in an insulated, water-tight, copper container in the thermostat at 25°. The entire measuring apparatus was protected from stray electrical effects by the equipotential shielding method recommended by White.²⁶

Experimental Data

The experimental values of the electromotive force at 25° are given in Table I, along with the value of the calculated function E'_0 . The observed electromotive force given in Column 3 is in each case the average of the six electrodes previously described. A correction for the solubility of lead sulfate is necessary at concentrations of 0.0056 molal and less. This was made by calculating the increase in sulfate-ion concentration in the solution arising from the solubility of the lead sulfate, and calculating the potential resulting therefrom. Böttger²⁷ reports the solubility of lead sulfate at 25° to be 1.34×10^{-4} , while Kohlrausch²⁸ finds 1.45×10^{-4} mole per liter. The value used in these calculations is the average, namely, 1.4×10^{-4} mole per liter. The Debye-Hückel theory gives 0.90 for f_{PbSO_4} at this concentration, assuming a value of 3 Å. for "a." Making use of f_{PbSO_4} , we find the activity solubility product of lead sulfate to be 1.59×10^{-8} . In order to calculate the increase in sulfate-ion concentration we made use of the equation

$$M_{\text{Pb}^{++}} \cdot f_{\pm} \cdot M_{\text{SO}_4}'' f_{\pm} = a_{\text{Pb}^{++}} \cdot a_{\text{SO}_4}''$$

or

$$M_{\text{Pb}^{++}} = \frac{K(a)}{M_{\text{SO}_4}'' \cdot (f_{\pm})^2}$$

By successive approximations the concentration of sulfate ion from the lead sulfate is found, since it is equal to the concentration of lead ion in the cadmium sulfate solution. The ideal individual ion potentials for the cadmium and sulfate ions are calculated in Columns 5 and 6. These two

²⁶ White, *THIS JOURNAL*, **36**, 2011 (1914).

²⁷ Böttger, *Z. physik. Chem.*, **46**, 604 (1903).

²⁸ Kohlrausch, *ibid.*, **64**, 129 (1908).

factors when added to the observed electromotive force give E'_0 (equation 9). Since these calculations were completed, another determination of the solubility of lead sulfate has been reported²⁹ which agrees very well with the results of Kohlrausch. If these calculations were to be repeated, even more weight would now be placed on the data of Kohlrausch. The effect on the final result is too small to make recalculation worth while.

Table II gives the experimental values of the electromotive force at 0° along with the calculated function E'_0 . The solubility of lead sulfate at 0° is 1.08×10^{-4} mole per liter. This value was obtained by plotting the data of Böttger²⁷ and Kohlrausch²⁸ as shown in Fig. 4 and extrapolating to the desired temperature, taking the average of the results thus obtained.

TABLE I
ELECTROMOTIVE FORCE OF THE CELL Pb-Hg (2 PHASE), PbSO₄ (s), CdSO₄, Cd-Hg (2 PHASE) AT 25°

No.	Molality of CdSO ₄	E , obs.	$M_{\text{SO}}^{\#}$ (total)	0.02957 log $M_{\text{Cd}^{++}}$	0.02957 log M'_{O_1}	E'_0
1	0.0004580	0.20241	0.0005043	-0.09875	-0.09752	+0.00614
2	.0005107	.20029	.0005536	- .09736	- .09632	+ .00661
3	.0005320	.19948	.0005737	- .09683	- .09586	+ .00679
4	.0006070	.19790	.0006451	- .09514	- .09436	+ .00840
5	.0007267	.19427	.0007604	- .09283	- .09224	+ .00920
6	.0008675	.19055	.0008972	- .09055	- .09012	+ .00988
7	.0009609	.18846	.0009886	- .08924	- .08887	+ .01035
8	.0009819	.18802	.001009	- .08896	- .08861	+ .01045
9	.001077	.18610	.001103	- .08777	- .08747	+ .01086
10	.001119	.18539	.001144	- .08728	- .08700	+ .01111
11	.001332	.18178	.001354	- .08504	- .08483	+ .01191
12	.001993	.17380	.002010	- .07987	- .07976	+ .01417
13	.002994	.16596	.003007	- .07464	- .07458	+ .01674
14	.003807	.16146	.003819	- .07155	- .07151	+ .01840
15	.004371	.15899	.004382	- .06978	- .06975	+ .01946
16	.005618	.15456	.005627	- .06656	- .06654	+ .02146
17	.007544	.14931	.007544	- .06277	- .06277	+ .02377
18	.007901	.14851	.007901	- .06218	- .06218	+ .02415
19	.008351	.14752	.008351	- .06146	- .06146	+ .02460
20	.009307	.14558	.009307	- .06007	- .06007	+ .02544
21	.009409	.14541	.009409	- .05993	- .05993	+ .02555
22	.01096	.14275	.01096	- .05797	- .05797	+ .02681
23	.02237	.13104	.02237	- .04881	- .04881	+ .03342
24	.05291	.11901	.05291	- .03775	- .03775	+ .04351
25	.1268	.10859	.1268	- .02653	- .02653	+ .05553
26	.3496	.09628	.3496	- .01350	- .01350	+ .06928
27	1.027	.08259	1.027	+ .00034	+ .00034	+ .08327
28	1.886	.07432	1.886	+ .00815	+ .00815	+ .09062
29	2.632	.06944	2.632	+ .01243	+ .01243	+ .09430
30	3.698 ^a	.04639	3.698	+ .01679	+ .01679	+ .09752

^a Saturated.

²⁹ Huybrechts and de Langeron, *Bull. soc. chim. Belg.*, 39, 43 (1930).

TABLE II
ELECTROMOTIVE FORCE OF THE CELL Pb-Hg (2 PHASE), PbSO₄ (s), CdSO₄ (M), Cd-Hg (2 PHASE) AT 0°

No.	Molality of CdSO ₄	E. obs.	M _{SO₄} ²⁻ (total)	0.02709 log M _{Cd²⁺}	0.02709 log M _{O₄} ²⁻	E ₀ '
1	0.0007267	0.19313	0.0007472	-0.08503	-0.08470	+0.02340
2	.0008675	.18969	.0008855	-.08294	-.08270	+ .02405
3	.001077	.18556	.001092	-.08040	-.08023	+ .02493
4	.001119	.18474	.001134	-.07995	-.07979	+ .02500
5	.001332	.18132	.001345	-.07790	-.07778	+ .02564
6	.001993	.17381	.002003	-.07316	-.07310	+ .02755
7	.002994	.16646	.003002	-.06837	-.06834	+ .02975
8	.003807	.16216	.003814	-.06554	-.06552	+ .03110
9	.004371	.15982	.004371	-.06392	-.06392	+ .03198
10	.005618	.15566	.005618	-.06096	-.06096	+ .03374
11	.007544	.15098	.007544	-.05750	-.05750	+ .03598
12	.007901	.15028	.007901	-.05695	-.05695	+ .03638
13	.009307	.14754	.009307	-.05502	-.05502	+ .03750
14	.01096	.14485	.01096	-.05310	-.05310	+ .03865
15	.05291	.12280	.05291	-.03458	-.03458	+ .05364
16	.1268	.11248	.1268	-.02430	-.02430	+ .06388
17	.3496	.10022	.3496	-.01236	-.01236	+ .07550
18	1.886	.07327	1.886	+ .00764	+ .00764	+ .08820
19	3.698	.05773	3.698	+ .01539	+ .01539	+ .08851

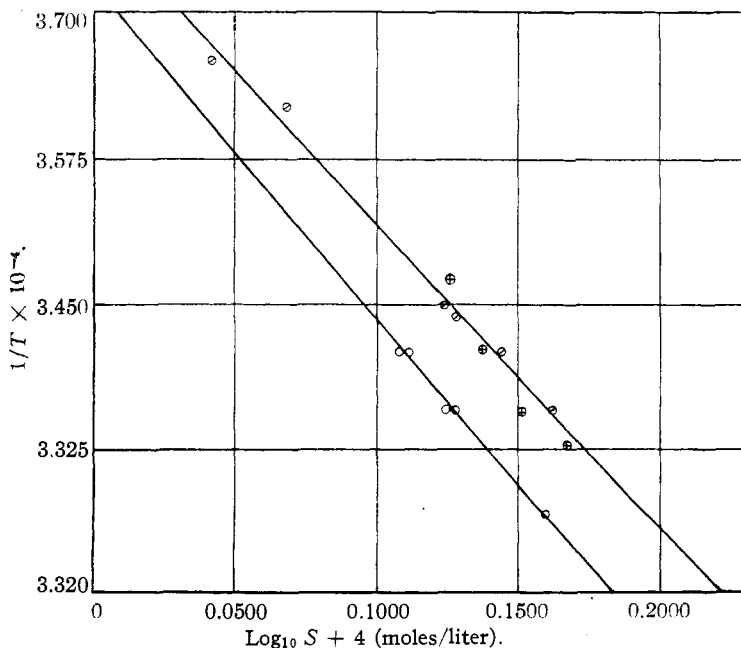


Fig. 4.—Solubility of lead sulfate in water. ⊖, Kohlrausch; ○, Böttger; ⊕, Huybrechts and de Langeron.

The data of Huybrechts and de Langeron are also given on this plot but were not used in the calculations. The Debye-Hückel theory gives 0.913 for f_{PbSO_4} at 0° , and the activity solubility product is 0.972×10^{-8} .

The values of E'_0 for dilute solutions at both temperatures (Tables I and II) are shown graphically in Fig. 5. The Debye-Hückel limiting law is shown by the broken line. The insert at the lower right-hand portion is for concentrated solutions and shows that the curves for 0 and 25° cross above 1 molal.

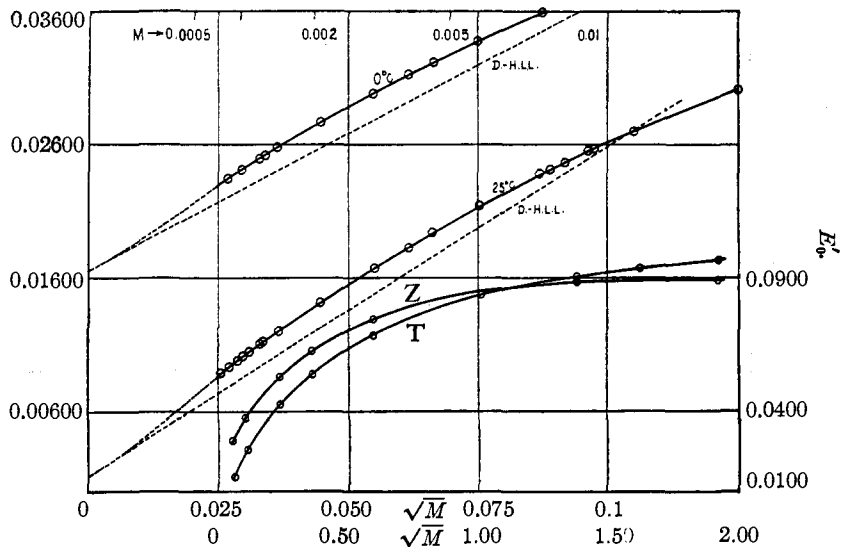


Fig. 5.—The cadmium-lead cell. T, 25° ; Z, 0° .

Discussion of Results

Table III gives the values of E_0 obtained when we insert the arbitrary values for " a " = 3, 3.6 and 4 Å. for cadmium sulfate in expression 6 in order to determine the value of $\log f$.

When the molality of cadmium sulfate is less than 0.0006 molal, the dissolved lead sulfate constitutes more than 6% of the total sulfate-ion concentration. At such very low concentrations of cadmium sulfate the cell can no longer be considered strictly as one without transfer and liquid junction potential, and the cell process would not correspond exactly to the one given in Equation 7. Since the experimental data were also somewhat erratic we have not included the first three measurements in our computations.

The values of E_0 computed in Table III are plotted in Fig. 6 as a function of \sqrt{M} . It is clearly evident that the correct value for E_0 is 0.00142 volt at 25° and that an ion size corresponding to " a " = 3.6 Å. yields values of E_0 having an average deviation of only 0.06 mv. for the nineteen determina-

TABLE III
VALUES OF E_0

No.	"a" = 3.0 Å.		"a" = 3.6 Å.		"a" = 4.0 Å.		
	E_0	Deviation from mean	E_0	Deviation from mean	E_0	Deviation from mean	
4	+0.00041	+0.00193	+0.00132	-0.00010	+0.00169	-0.00084	
5	+ .00037	+ .00189	+ .00143	+ .00001	+ .00185	- .00068	
6	+ .00015	+ .00167	+ .00137	- .00005	+ .00186	- .00067	
7	+ .00007	+ .00149	+ .00138	- .00004	+ .00191	- .00062	
8	+ .00004	+ .00146	+ .00138	- .00004	+ .00192	- .00061	
9	- .00008	+ .00144	+ .00136	- .00006	+ .00194	- .00059	
10	- .00005	+ .00147	+ .00143	+ .00001	+ .00202	- .00051	
11	- .00042	+ .00110	+ .00135	- .00007	+ .00202	- .00051	
12	- .00086	+ .00066	+ .00136	- .00006	+ .00224	- .00029	
13	- .00153	- .00001	+ .00134	- .00008	+ .00246	- .00007	
14	- .00196	- .00044	+ .00133	- .00009	+ .00261	+ .00008	
15	- .00214	- .00062	+ .00139	- .00003	+ .00276	+ .00023	
16	- .00248	- .00096	+ .00150	+ .00008	+ .00304	+ .00051	
17	- .00299	- .00147	+ .00150	+ .00008	+ .00322	+ .00069	
18	- .00306	- .00154	+ .00151	+ .00009	+ .00326	+ .00073	
19	- .00315	- .00163	+ .00151	+ .00009	+ .00329	+ .00076	
20	- .00335	- .00183	+ .00147	+ .00005	+ .00331	+ .00078	
21	- .00335	- .00183	+ .00149	+ .00007	+ .00334	+ .00081	
22	- .00356	- .00204	+ .00149	+ .00007	+ .00342	+ .00089	
23	- .00365	+ .00198	+ .00421	
Mean =	-0.00152		Mean =	+0.00142	= 0.00006	Mean =	+0.00253

tions extending from 0.000670 to 0.01096 molal. The maximum deviation is 0.1 mv. for the measurement corresponding to $M = 0.000670$.

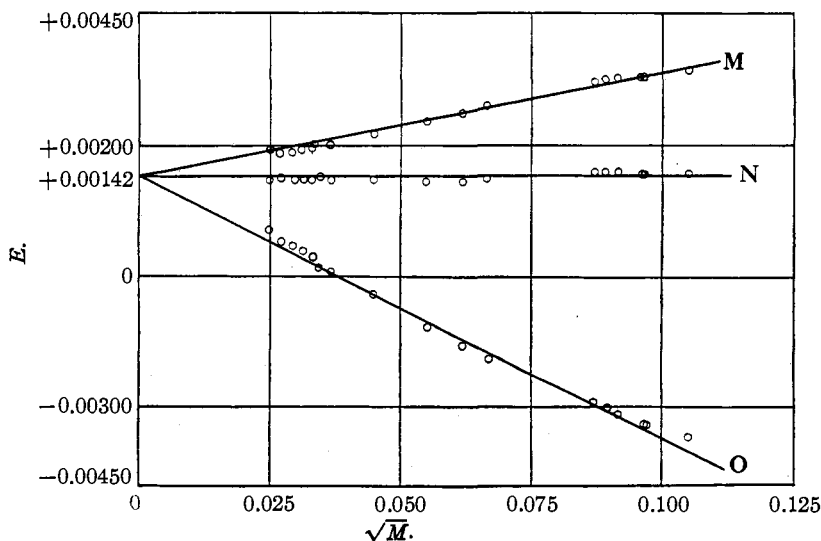


Fig. 6.—M, 4.0 Å.; N, 3.6 Å.; O, 3.0 Å.

In other words, E_0 is constant within the limits of experimental error under the assumption " a " = 3.6 Å., whereas the values of E_0 drift when other values of " a " are employed in Equation 6. Had we extrapolated the E'_0 , \sqrt{M} curve in Fig. 6 to zero concentration using a Debye limiting law slope passing through the points of lowest concentration, as previous investigators have done, we would obtain the erroneous value $E_0 = 0.00180$ volt, differing from our E_0 by 0.00038 volt, which is about six times the experimental error. The apparent slope of the E'_0 against \sqrt{M} curve at 25° between $M = 0$ to $M = 0.0006$ is 0.275 instead of 0.239 as predicted by the Debye limiting law (equation 11), and emphasizes that this law is not obeyed even at such a low concentration range.

In Table IV are given the calculated values of " a " both from the Debye approximation [$-\log f = 1.53636z^2\kappa/(1 + \kappa'a')$] and the Gronwall, La Mer and Sandved extension⁵ through a fifth approximation.

TABLE IV

COMPARISON OF THE " a " VALUES FOR CADMIUM SULFATE AT 25° COMPUTED FROM THE DEBYE AND FROM THE FIFTH APPROXIMATION ($E_0 = 0.00142$)

No.	Molality	" a " (Debye), Å.	" a " (fifth approx.), Å.
4	0.0006070	-9.74	+3.72
5	.0007267	-9.78	+3.64
6	.0008675	-8.74	+3.68
7	.0009609	-8.43	+3.68
8	.0009819	-8.35	+3.68
9	.001077	-7.90	+3.68
10	.001119	-8.02	+3.60
11	.001332	-7.08	+3.64
12	.001993	-5.58	+3.62
13	.002994	-4.11	+3.61
14	.003807	-3.28	+3.61
15	.004371	-2.89	+3.60
16	.005618	-2.18	+3.56
17	.007544	-1.27	+3.52
18	.007901	-1.14	+3.56
19	.008351	-0.98	+3.56
20	.009307	-.65	+3.52
21	.009409	-.64	+3.52
22	.01096	-.23	+3.52
23	.02237	+1.18	+3.04

It is readily seen that the Debye approximation gives values for " a " (Column 3) which drift steadily from -9.78 to -0.23 Å. at 0.01 molal. These values are physically absurd. On the other hand, use of the higher terms gives constant, physically plausible, positive values of " a " as shown in Column 4. The slight drift in these values of " a " may be due to neglecting the seventh approximation. These data (Table IV), although they emphasize the inadequacy of the Debye approximation in dilute solution

in a very striking manner, nevertheless confirm in an equally striking manner the validity of the basic assumptions of the theory when given simply the more complete mathematical treatment.

From a large scale plot of E'_0 against \sqrt{M} , values of E'_0 at round concentrations were read, and the corresponding activity coefficients were calculated by Equation 10, using the value of E_0 obtained by extrapolation. These values are given in Table V along with the activity coefficients calculated from the theory.

TABLE V
THE ACTIVITY COEFFICIENTS OF CADMIUM SULFATE AT 25°

No.	Molality	Calculated activity coefficient (equation (5), "a" = 3.6 Å.)	Observed activity coefficient (from e. m. f., equation (10)) $E_0 = 0.00142$	Difference
1	0.0005	0.775	0.774	-0.001
2	.001	.700	.699	- .001
3	.003	.549	.551	+ .002
4	.005	.476	.476	± .000
5	.01	.384	.383	- .001
6	.03	.265	.254	- .011
7	.05	.220	.199	- .021
8	.1	.166	.137	- .029
9	.5		.0605	
10	1.0		.0418	
11	1.5		.0385	
12	2.0		.0304	
13	2.5		.0282	
14	3.0		.0261	
15	3.5		.0260	

Up to 0.01 molal (ionic strength of 0.04) the agreement is within 0.4%, which is well within the experimental error. This is striking when one considers that even at 0.01 molal the activity coefficient has fallen to 0.383.

The results obtained by repeating this method of extrapolation for E_0 at 0° are summarized in Table VI and are shown graphically in Fig. 7. Evaluating the constants in Equation 5 for use at 0° we obtain the following

$$-\log f = \frac{z^2}{a} 1.49701 \frac{x}{1+x} - \left(\frac{z^2}{a}\right)^3 0.142297 \cdot 10^3$$

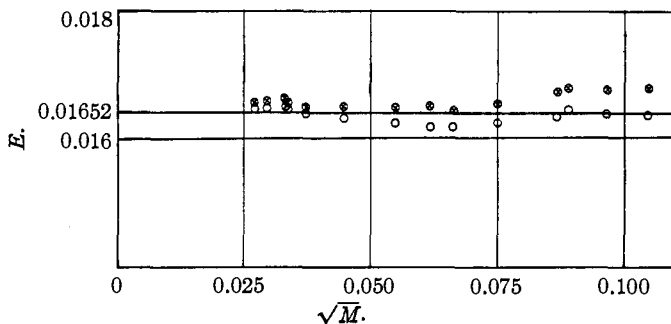
$$\left[\frac{1}{2} X_3(x) - 2Y_3(x)\right] - \left(\frac{z^2}{a}\right)^5 0.06763 \cdot 10^5 \left[\frac{1}{2} X_5(x) - 4Y_5(x)\right] \quad (15)$$

The best value for "a" at this temperature is certainly between 3.6 and 3.7 Å. The change in "a" from 25 to 0° is then less than 0.1 Å., which means that $(\partial "a" / \partial T)$ is very small, that is, of the order of 0.004 Å. per degree as a maximum. As far as we are aware this is the first time that $(\partial "a" / \partial T)$ has been determined directly in a region of concentration where it can be interpreted theoretically. The fact that $(\partial "a" / \partial T)$ for cadmium

TABLE VI
 CALCULATED VALUES

No.	"a" = 3.6 Å.		"a" = 3.7 Å.	
	E_0	Deviation from mean	E_0	Deviation from mean
1	+0.01666	+0.00012	+0.01676	-0.00004
2	+ .01667	+ .00013	+ .01679	- .00001
3	+ .01670	+ .00018	+ .01683	+ .00003
4	+ .01661	+ .00009	+ .01675	- .00005
5	+ .01650	- .00002	+ .01665	- .00015
6	+ .01645	- .00007	+ .01666	- .00014
7	+ .01639	- .00012	+ .01666	- .00014
8	+ .01628	- .00022	+ .01668	- .00012
9	+ .01628	- .00022	+ .01661	- .00019
10	+ .01638	- .00014	+ .01674	- .00006
11	+ .01657	+ .00005	+ .01698	+ .00018
12	+ .01664	+ .00012	+ .01706	+ .00026
13	+ .01658	+ .00006	+ .01703	+ .00023
14	+ .01652	± .00000	+ .01700	+ .00020
	Mean = 0.01652		Mean = 0.01680	

sulfate is virtually zero lends support to the hypothesis that the value "a" is primarily a measure of the distance of closest approach of the ions without including their surrounding shells of polarized water molecules. Otherwise, larger values of "a" would be demanded which should decrease with rising temperature owing to decreasing hydration.^{30a}


 Fig. 7.—O, $a = 3.6 \text{ \AA.}$; \otimes , $a = 3.7 \text{ \AA.}$

A comparison of the experimental and theoretical activity coefficients at round concentrations is given in Table VII. The agreement is satisfactory to concentrations including 0.01 molal.

Gronwall, La Mer and Sandved⁵ found for Bray's data on zinc sulfate that Equation 5 does not fit the experimental data when M exceeds 0.01096 or κ exceeds 0.0687. Tables III and VI show that the same is true for cadmium sulfate. There are several reasons for this failure of Equation 5 to hold above this concentration. First, this concentration corresponds

³⁰(a) Bjerrum, *Trans. Faraday Soc.*, **23**, 445 (1927); (b) *Ber.*, **62**, 1091 (1929).

TABLE VII
THE ACTIVITY COEFFICIENTS OF CADMIUM SULFATE AT 0°

No.	Molality	Calculated activity coefficient (eq. (15), "a" = 3.6 Å.)	Observed activity coefficient (from e. m. f., eq. (10)) $E_0 = 0.01652$	Difference
1	0.0005	0.786	0.779	-0.0007
2	.001	.714	.710	-.004
3	.005	.494	.494	= .000
4	.01	.402	.399	-.003
5	.05	.232	.217	-.015
6	.1	.176	.149	-.027
7	.5		.0734	
8	1.0		.0574	
9	2.0		.0484	
10	3.0		.0475	

to a value of $x = "a" \times \kappa = 3.6 \times 0.0687 = 0.25$. Although a 0.01 *M* or 0.04 μ solution is ordinarily considered a quite dilute solution from a chemist's standpoint, nevertheless it is concentrated from the standpoint of the Debye-Hückel theory. Thus, when x reaches a value of 0.25 the fundamental approximations of the theory certainly can no longer hold exactly, for this value of x means that $1/\kappa$, namely, the distance from a given ion at which the electric potential due to the ion atmosphere has fallen to $1/e$ of its value at the distance $r = "a,"$ is equal to four times the value of " a ." Secondly, a comparison of Equation 5 with the unabridged Equation (34a) of Gronwall, La Mer and Sandved⁵ shows that each approximation contains the factor $\left(1 - 10^{-3}c \frac{\partial V}{\partial n}\right) \left(1 - \frac{cdD}{Ddc}\right)$. The quantity $\left(1 - 10^{-3}c \frac{\partial V}{\partial n}\right)$ is known to be negligible in dilute solutions, but the quantity $\left(1 - \frac{cdD}{Ddc}\right)$ representing the change in dielectric constant with concentration is very likely not equal to unity at concentrations above 0.01 molal. Unfortunately, no one has succeeded as yet in measuring accurately the dielectric constant of conducting solutions at appreciable concentrations.³¹ Until this question has been defined and settled experimentally one must make the approximation that $\left(1 - \frac{cdD}{Ddc}\right)$ is equal to unity, with the result that we cannot expect Equation 5 to hold precisely above 0.01 molal.

To avoid misunderstanding it is important to emphasize that the assumption $\left(1 - \frac{c}{D} \frac{dD}{dc}\right) = 1$ is equivalent to the customary one that $D = D_0$ where the subscript zero refers to the pure solvent. The major effect of this assumption will usually reside in the first approximation and not in the higher terms, *i. e.*, in the difference between the first and last terms of Equation 34a of Reference 5. The unabridged Equation 34a thus embodies

³¹ Debye, "Polar Molecules," Chemical Catalog Co., Inc., New York, 1929, p. 124.

the well-known dielectric correction suggested by Hückel [*Physik. Z.*, **26**, 93-147 (1925)] but does it in a more general manner since no restrictions, such as the linear variation of D with c assumed by Hückel, are made in obtaining the final equation. To employ 34a it will be necessary to know D and dD/dc only at the concentration in question.

Other factors such as the employment of local smoothing in calculating the charge density, the forces resulting from the deformability of the ions and the interpretation of the dielectric constant in the neighborhood of an ion undoubtedly influence the value of " a " computed by equations (6)₂₅ and (15)₀. However, unless some peculiar and unlikely effects are just compensating one another in the case of cadmium sulfate as well as for zinc sulfate,³² it hardly seems necessary to take the extreme view given by Fowler³³ that " a " is only an "*omnium gatherum*" correction and does not have the significance of an ionic diameter. The evidence now at hand indicates that this viewpoint and the one by Bjerrum,^{30b} namely, that " a " is "stark temperatur empfindlich" appear to have been based too much

TABLE VIII

PARTIAL MOLAL FREE ENERGY OF TRANSFER OF CADMIUM SULFATE AT 25°

Concn., M_1	Concn., M_2	ΔE	$\Delta\bar{F}$ (obs.), cal.	$\Delta\bar{F}$ (excess), cal.
3.0	2.0	0.00606	+280	+ 40
2.0	1.0	.00966	+446	+ 35
1.0	0.1	.02865	+1322	- 43
0.5	.05	.02807	+1295	- 80
.1	.01	.03271	+1510	+145
.05	.005	.03672	+1695	+330
.03	.003	.03915	+1807	+442
.01	.001	.04334	+2000	+635
.005	.0005	.04557	+2103	+738

TABLE IX

PARTIAL MOLAL FREE ENERGY OF TRANSFER OF CADMIUM SULFATE AT 0°

Concn., M_1	Concn., M_2	ΔE	$\Delta\bar{F}$ (obs.), cal.	$\Delta\bar{F}$ (excess), cal.
3.0	2.0	0.00887	+ 409	+189
2.0	1.0	.01233	+ 569	+193
1.0	0.1	.03147	+1450	+200
0.5	.05	.02851	+1317	+ 67
.1	.01	.03103	+1432	+182
.05	.005	.03481	+1606	+356
.01	.001	.04045	+1867	+617
.005	.0005	.04284	+1977	+727

³² Cowperthwaite and La Mer (to be published) in their studies on the corresponding zinc sulfate cell find the following values for " a ": 3.6 Å. (0°), 3.64 Å. (12.5°), 3.64 Å. (25°), 3.60 Å. (37.5°), 3.73 Å. (50°).

³³ Fowler, "Statistical Mechanics," Cambridge University Press, London, 1929, p. 322.

upon results obtained by using the Debye approximation without giving sufficient weight to the contribution of the higher approximations. It will be highly important to ascertain what the same simple state of affairs obtains for the "a" value of other 2-2 electrolytes.

In Table VIII are given the calculated values of the free energy of transfer of one mole of cadmium sulfate from concentration M_1 to concentration M_2 at 25°. The excess free energy of transfer is given in Column 5. Table IX gives the corresponding values at 0°.

The Gibbs-Helmholtz Equation (14) enables one to calculate the heats of transfer arising from electrical interaction. Substituting for E in (14) its value

$$E = E_0 - \frac{RT}{nF} \ln M - \frac{RT}{nF} \ln f \quad (16)$$

we get

$$-\Delta H = nF \left[E_0 - T \frac{\partial E_0}{\partial T} + \frac{RT^2}{nF} \frac{\partial \ln f}{\partial T} \right] \quad (17)$$

Now

$$E'_0 = E_0 - \frac{RT}{nF} \ln f \quad (18)$$

so Equation 17 can be written in a form more directly applicable to the experimental data, namely

$$-\Delta H = nF \left[E'_0 - T \frac{\partial E'_0}{\partial T} \right] \quad (19)$$

Since measurements were made at only two temperatures we are obliged to assume that $(\Delta E/\Delta T)_M = (\partial E/\partial T)_M$, an approximation which will be most nearly correct for 12.5°. We have therefore calculated the *mean* heat of transfer for the total process (7) defined as

$$\begin{aligned} -\Delta H_{285.6} &= nF \left[\frac{E'_{0(25^\circ)} + E'_{0(0^\circ)}}{2} - T \frac{E'_{0(25^\circ)} - E'_{0(0^\circ)}}{25} \right] \\ &= nF \left[E'_{0(12.5^\circ)} - T_{285.6} \frac{\Delta E'_0}{\Delta T} \right] \end{aligned} \quad (20)$$

These values are given in Table X, Column 6.

When $M = 0$, Equation 20 gives $-\Delta H_{285.6}^0 = 8375$ cal., that is, the value of $-\Delta H$ for the total process (7), which is free from any contribution due to electrical interaction.

In Column 7 (Table X) we give the values of the excess or electrical partial molal heat of transfer $-\bar{H}_{(e)}$, defined as

$$-\Delta H - (-\Delta H^0) = \bar{H}_{\text{CdSO}_4} - \bar{H}_{\text{CdSO}_4}^0 = -\bar{H}_{(e)} \quad (21)$$

$(-\bar{H}_{(e)})$ is the quantity of heat which is liberated by the forces of electrical interaction when one mole of cadmium sulfate is reversibly transferred from a very large volume of solution of molality M to a similar volume of solution where M equals zero.

TABLE X
CALCULATED VALUES

No.	Molality of CdSO ₄	$E'_0(25^\circ)$	$E'_0(0^\circ)$	$E'_0(25) - E'_0(0^\circ)$	$-\Delta H_{(25,0)}$, cal.	$-\Delta \bar{H}_{(e)}$, cal.
1	0.0000	0.00142	0.01652	-0.01510	+8375	...
2	.0005	.00795	.02235	-.01440	+8291	+ 84
3	.001	.01062	.02458	-.01396	+8167	+ 208
4	.002	.01415	.02754	-.01339	+8026	+ 349
5	.005	.02050	.03313	-.01263	+7893	+ 482
6	.01	.02607	.03813	-.01206	+7834	+ 541
7	.02	.03224	.04300	-.01076	+7403	+ 972
8	.05	.04290	.05250	-.00960	+7262	+1113
9	.1	.05250	.06123	-.00873	+7224	+1151
10	.5	.07398	.07816	-.00418	+5712	+2663
11	1.0	.08300	.08400	-.00100	+4381	+3994
12	2.0	.09115	.08796	+.00319	+2446	+5929
13	3.0	.09550	.08851	+.00699	+ 555	+7820

The values of $-\Delta \bar{H}_{(e)}$ are plotted as a function of \sqrt{M} in Fig. 8.

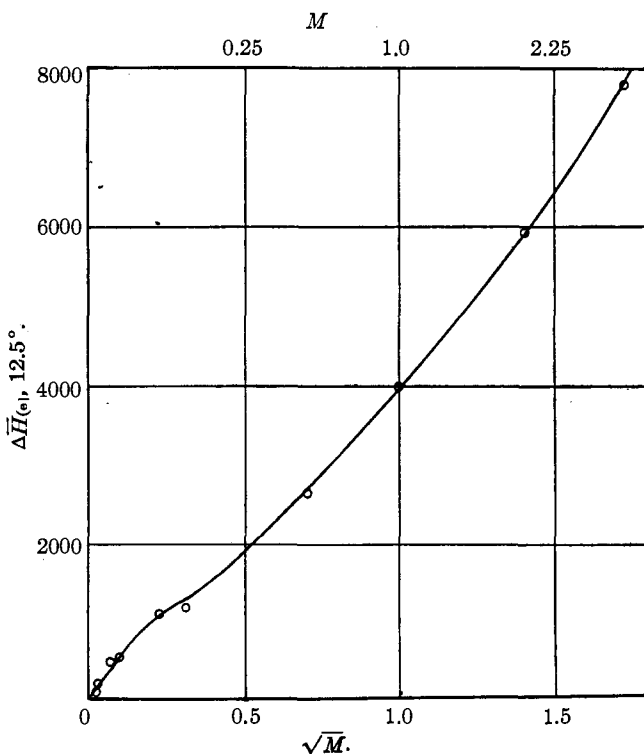


Fig. 8.

Summary

Precise electromotive force measurements are reported at 25 and 0° for the cell Cd-Hg (2 phase), CdSO₄ (M), PbSO₄ (s), Pb-Hg (2 phase) over the

concentration range 0.0004580 to 3.698 molal. The potential of the cell (E_0) when the ion activities of cadmium sulfate are hypothetically one molal has been found to be 0.00142 volt at 25° and 0.01652 volt at 0°.

The experimental results furnish excellent confirmation of the extension of the Debye-Hückel theory as given by Gronwall, La Mer and Sandved for the region 0.0006 to 0.01 molal, since their extension yields constant and positive, physically plausible values of " a " (3.6 Å.) where " a " is the distance of closest approach of the ions. The Debye-Hückel approximation gives steadily drifting and physically absurd, negative values of " a ." This extension furnishes an excellent control on the extrapolation to infinite dilution, since constant values for E_0 are obtained up to 0.01 molal.

The activity coefficients and the partial molal free energies of transfer of cadmium sulfate have been computed at 25 and 0° for the concentration range 0.0005 molal to saturation.

If cadmium sulfate is incompletely dissociated in the classical sense, this influence on the activity coefficient is too small to be detected below 0.01 molal.

It has been shown by direct measurement that $(\partial'a''/\partial T)$ is very small, if not actually zero. This may be taken as support for the view that hydration of the ions is not involved in the value " a ."

The mean heat of the cell reaction, Cd (solid, satd. with Hg) + PbSO₄ (solid) = CdSO₄ (M) + Pb (solid, satd. with Hg), for 12.5° and the corresponding excess electrical heats of transfer of cadmium sulfate have been computed using the Gibbs-Helmholtz equation.

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THE THERMAL DECOMPOSITION OF DIMETHYL-TRIAZENE. A HOMOGENEOUS UNIMOLECULAR REACTION

BY H. C. RAMSPERGER AND J. A. LEERMAKERS

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During the past four years a considerable amount of experimental data has given support to certain theories of unimolecular reaction velocity which postulate that activation occurs by kinetic theory collisions. The rate of production of activated molecules by collisions is a second order process but if only a very small fraction of those molecules which become activated decompose spontaneously the rate of decomposition is first order. At sufficiently low pressures collisions can no longer maintain the Maxwell-Boltzmann quota of activated molecules; consequently the rate falls off until finally at still lower pressures the rate approaches the rate of activation and is second order.