only the valence of the ions, the viscosity and dielectric constant of the solvent, and certain other physical factors are involved. If we wish to investigate whether or not in an ionic solution the chemical nature of the solvent and the affinities of ions play an important role, experiments of the type described above in which these factors are varied can give valuable information. In the experiments here reported a nearly ideal ionic behavior is observed, but it is probably accounted for because only extremely dilute aqueous solutions were considered. But even if the chemical nature of the solvent and the affinities of the ions are predominant factors, such experiments as these are still of significance because they explain and predict the behavior of ideal electrolytes and make possible a measure of the deviations from ideality in the actual solution.

Summary

1. A quantitative experimental study of the dispersions of the electrical conductance for strong electrolytes of several valence types in extremely dilute aqueous solutions has been made. The conductance of these solutions was observed at frequencies corresponding to the seven wave lengths, 15, 30, 50, 75, 100, 130 and 170 meters. In addition, observations were made at the frequency 1000 cycles.

2. The results of the experiments have been compared with the requirements of the dispersion theory. They are found to be in satisfactory quantitative agreement, indicating once more that in all probability the purely physical interionic attraction theory does adequately explain and describe the behavior of an ideal electrolyte.

MADISON, WIS. RECEIVED AUGUST 17, 1936

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, YALE UNIVERSITY]

The Thermodynamics of Cadmium Chloride in Aqueous Solution from Electromotive Force Measurements[1]

BY HERBERT S. HARNED AND MARGARET E. FITZGERALD

Measurements of the electromotive forces of the cell

$$\mathrm{Cd{-}Cd_xHg}\ (11\%)\ |\ \mathrm{CdCl_2}(m)\ |\ \mathrm{AgCl{-}Ag} \qquad (1)$$

have been made at 5° intervals from 0 to 40°, inclusive, and throughout a cadmium chloride concentration range of 0.0005 to 1 *M*. From the results, the standard potential of the cell, E_0, the activity coefficients and other thermodynamic properties of cadmium chloride have been computed.

Experimental Procedure

The silver–silver chloride electrodes of the kind designated by Harned[2] as type (2) were used. The cadmium amalgam was prepared from pure redistilled Kahlbaum cadmium and distilled mercury. The amalgam electrodes containing 11% of total cadmium were made individually in each cell vessel.

Mercury and an excess of cadmium were introduced in a suitable glass vessel which was then evacuated. This mixture was placed in a water-bath at 60° for fifteen minutes, and was shaken frequently. The saturated amalgam formed in this manner was allowed to flow through a sealed tube into the amalgam electrode compartments of four cells where it covered the sealed in platinum wires which made contact with the external leads. Since this operation was carried out *in vacuo*, the amalgam was free of oxide. In the case of cells containing dilute solutions ($m < 0.05$ *M*) the silver chloride electrode was immersed in the same compartment as the amalgam. On the other hand, with higher concentrations of solution the life of the cell was found to be considerably increased by separating the electrode compartments by means of a tube and a stopcock which was closed at times when actual measurements were not in progress.

A standard concentrated stock solution was made from a high-grade carefully purified cadmium chloride and conductivity water. Its strength was found by gravimetric determination of its chloride content. More dilute solutions were prepared by adding weighed amounts of the standard solution to water. The cell solu-

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(1) This communication contains material from a Dissertation presented to the Graduate Faculty of Yale University in partial fulfilment of the requirements for the degree of Doctor of Philosophy, June, 1936.

(2) Harned, THIS JOURNAL, **51**, 416 (1929).

tions were then boiled *in vacuo* to remove dissolved air, and kept under hydrogen. Corrections were made for the water boiled off during this process and vacuum corrections were made for all weighings.

The cells came to equilibrium in one to two hours after preparation. Four cells were measured at each concentration. The temperature control was within ±0.02°.

Experimental Results

Electromotive forces were determined at thirty-odd concentrations ranging from 0.0005 to 1 M and at 5° intervals from 0 to 40°. These were smoothed to round concentrations from a graph of E *versus* log m. The actual values may be expressed conveniently by means of the quadratic equation

$$E = E_{25} + a(t - 25) + b(t - 25)^2 \qquad (2)$$

Values of E_{25}, a and b are given in Table I. In the last column are given the average deviation between the observed results and those computed by the equation. In other words, Δ is the sum of the magnitudes of deviations at the nine temperatures divided by nine.

TABLE I

CONSTANTS OF EQUATION (2)

E = Electromotive Force of the Cell: $Cd{-}Cd_xHg \mid CdCl_2(m) \mid AgCl{-}Ag$

m	E_{25}	$a \times 10^6$	$b \times 10^6$	Δ, mv.
0.0005	0.8539	560	−3.48	0.14
.001	.82997	494	−3.40	.10
.002	.80701	430	−3.30	.06
.005	.77851	356	−3.13	.18
.007	.76862	338	−3.02	.07
.01	.75846	305	−2.93	.07
.02	.73976	242	−2.55	.11
.05	.71739	185	−2.05	.04
.07	.70974	161	−1.88	.05
.1	.70175	136	−1.68	.06
.2	.68656	104	−1.30	.09
.5	.66864	48	−0.80	.13
.7	.66258	29	− .62	.08
1.0	.65640	12	− .44	.15
	$E_{0(25)}$	$a_0 \times 10^6$	$b_0 \times 10^6$	
E_0:	.57390	−394	−3.63	.09

Similar cells have been measured at 25° by Horsch,[3] Lucasse[4] and from 0 to 45° by Quintin.[5] Since Horsch and Lucasse used amalgams of different compositions which were unsaturated, the absolute values of their electromotive forces are different from the present results. Graphs of the data of Horsch, Lucasse and the present results *versus* log m were found to be parallel, which indicated the same effect of change in concentration in all cases. Lucasse did not state the strength of the amalgam employed. The explanation of the difference between our results and those of Horsch is due not only to the difference in amalgam strength but also to the fact that Horsch employed silver–silver chloride electrodes prepared in the manner described by Lewis and Brighton.[6] These were found to be several millivolts different from the type of electrode employed by us. On the other hand, our results are in close agreement with those of Quintin who also employed the saturated amalgam.

The experimental accuracy was in general of the order of 0.1 mv. At the higher concentrations (> 0.1 M), the experimental error was found to be somewhat greater than this.

Evaluation of the Standard Potential of the Cell

The electromotive force of the cell may be represented by the equation

$$E = E_0 - k \log 4m^3\gamma_{\pm}{}^3 \qquad (3)$$

where E_0 is the standard potential, m and $\gamma_{\pm}$ are the molality and stoichiometrical activity coefficient of cadmium chloride and k equals 2.303 $RT/2F$. By replacing log $\gamma_{\pm}$ by $(-\mu\sqrt{m} + B'm)$ where μ is the limiting slope of the Debye and Hückel theory, we obtain

$$E + k \log 4m^3 = 3ku\sqrt{\mu} = E_0 - B'm = E_H \qquad (4)$$

The left-hand side, plotted against $\sqrt{m}$, was found to give a curve at all temperatures of which the slope increased with decreasing concentration. The data of Horsch in very dilute solutions at 25° was plotted in this way and although a fairly representative straight line could be drawn, the uncertainty of this method of extrapolation was great. Further, these graphs possessed slopes about twice that predicted by theory. This uncertainty is shown by earlier extrapolations. Getman[7] plotted this function against $\sqrt{\mu}$, using Horsch's data and found E_0 to be 0.6215. La Mer, Gronwall and Greiff[8] plotted the same data against $\sqrt{m}$ and obtained 0.5790 for E_0 but did not consider this a proper value. Instead they applied their extension of the Debye and Hückel

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(3) Horsch, THIS JOURNAL, **41**, 1787 (1919).

(4) Lucasse, *ibid.*, **51**, 2597 (1929).

(5) Quintin, *Compt. rend.*, **200**, 1579 (1935).

(6) Lewis and Brighton, THIS JOURNAL, **39**, 1908 (1917).

(7) Getman, *J. Phys. Chem.*, **35**, 588 (1931).

(8) La Mer, Gronwall and Greiff, *ibid.*, **35**, 2245 (1931).

theory using an apparent ionic diameter "a" of 1 Å., and obtained 0.6230 for E_0.

According to equation (4), if cadmium chloride were a completely dissociated electrolyte, a plot of $E + k \log 4m^3 - 3k\mu\sqrt{m}$ should be linear with m in dilute solutions. That this is not the case confirms the view derived from conductance data that cadmium chloride is incompletely dissociated.

The dissociation mechanism which from the character of the data appears to be most suitable is

$$\mathrm{CdCl_2} = \mathrm{Cl^-} + \mathrm{CdCl^+} \rightleftharpoons \mathrm{Cd^{++}} + \mathrm{Cl^-} \qquad (5)$$

according to which cadmium chloride is completely dissociated while the ion $\mathrm{CdCl^+}$ is partially dissociated. It is probable that both cadmium chloride and $\mathrm{CdCl^+}$ are incompletely dissociated. The above assumption neglects the first dissociation as having a negligible effect compared to the second in dilute solution. If α is the degree of dissociation of $\mathrm{CdCl^+}$ and K the dissociation constant of this equilibrium, then the former is given by the equation

$$\alpha = \frac{1}{2}\left\{ -\left(1 + \frac{K}{m\gamma'_{\mathrm{Cd}}}\right) + \sqrt{\left(1 + \frac{K}{m\gamma'_{\mathrm{Cd}}}\right)^2 + 4\,\frac{K}{m\gamma'_{\mathrm{Cd}}}} \right\} \qquad (6)$$

if γ^1_{Cl} is assumed to equal γ'_{CdCl}.

Some idea of the magnitude of K may be gained by considering the conductance data of Wershoven[9] at 18°, from which Noyes and Falk[10] calculated degrees of dissociation. These estimates place K between 0.007 and 0.02. From the same data, Reghellato and Davies[11] found, by means of Onsager's theory and by assuming a reasonable value for the mobility of the ion $\mathrm{CdCl^+}$, an equilibrium constant of 0.0101 at 25°.

Our first step was to compute α by equation (6) for values of K in the neighborhood of 0.01 (0.005 to 0.015). γ'_{Cd} was computed from the Debye and Hückel equation

$$\log \gamma'_{\mathrm{Cd}} = -2u\sqrt{\mu'}/(1 + A\sqrt{\mu'}) \qquad (7)$$

employing a value of the mean apparent diameter "a" of 5 Å. The primed quantities are real, while the unprimed quantities are stoichiometrical. Thus, μ' is $\Sigma m_i' z_i^2/2$ where m_i' represents the actual ionic concentrations. This required the following procedure. An initial value of α was assumed for values of K and m under consideration. From this, μ' was calculated from the relation

$$\mu' = (2\alpha + 1)m \qquad (8)$$

and γ'_{Cd} was obtained by equation (7). Then α was recalculated by equation (6) using this value of γ'_{Cd}. From this value of α another γ'_{Cd} and μ' were found, and equation (7) applied again. This process was repeated until the same value of α, to a few ten thousandths of a unit, was obtained twice. This procedure was carried out at 0, 25 and 40° to obtain values of α from 0.0005 to 0.5 M with various values of K.

Equation (3) is written in terms of the stoichiometric activity and coefficients and molality. It may also be written in terms of the real activity coefficient $\gamma'_\pm$ and actual ionic concentrations in the form

$$E = E_0 - k \log \alpha(1 + \alpha)^2 m^3 \gamma_\pm^3 \qquad (9)$$

From the definition of E_{H} in equation (4) ,we have

$$E_{\mathrm{H}} - E_0 = E - E_0 + k \log 4m^3 - 3\,ku\sqrt{\mu} \qquad (10)$$

which combined with equation (9) gives

$$E_{\mathrm{H}} - E_0 = k \log 4 - \log \alpha(\alpha + 1)^2 - 3k \log \gamma' - 3ku\sqrt{\mu} \qquad (11)$$

The right side of this latter equation was computed for various values of K and plotted against $\sqrt{m}$, using the activity coefficient of barium chloride obtained by Tippetts and Newton[12] for the real activity coefficient of cadmium chloride, $\gamma'_\pm$. This substitution is a reasonable one in dilute solutions and increases in validity with decreasing concentration. In Fig. 1 the general form of these curves are illustrated by the smooth lines.

The function, E_{H}, computed from E by equation (4) was then plotted for 0, 25 and 40° against $\sqrt{m}$ and compared to the curves calculated by equation (11) and for values of K varied by one thousandth unit. In Fig. 1 plots of this function are shown together with the curves which fitted them best. The values of the dissociation constants employed finally were 0.013, 0.011 and 0.010 at 0, 25 and 40°, respectively. The values of the right-hand member of equation (11) were read off the curves and subtracted from the original unsmoothed E_{H} functions. According to equations (10) and (11), this gave

$$E_0 = E + k \log \alpha(1 + \alpha)^2 m^3 \gamma'^3_\pm \qquad (12)$$

The values of E_0 obtained in this manner were averaged by drawing a straight line of zero slope through the points obtained by plotting against $\sqrt{m}$. The actual plots of these functions com-

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[9] Wershoven, *Z. physik. Chem.*, **5**, 481 (1890).

[10] Noyes and Falk, THIS JOURNAL, **34**, 475 (1912).

[11] Reghellato and Davies, *Trans. Faraday Soc.*, **26**, 592 (1930).

[12] Tippetts and Newton, THIS JOURNAL, **56**, 1675 (1934).

puted from the unsmoothed electromotive forces are also shown in Fig. 1.

In order to obtain E_0 at the other temperatures, the correction factors, $E_H - E_0$, used for each concentration at 0, 25 and 40° were plotted against temperature and smoothed curves drawn through three points. The correction factors read from these curves at the intermediate temperatures were then applied in the manner previously described to E_H, and the values of E_0 so obtained were averaged. These standard potentials are given in the second column of Table II.

TABLE II

STANDARD POTENTIALS OF:

$Cd-Cd_xHg$ (11%)|$CdCl_2$ (m)|AgCl–Ag; E_0

$Cd-Cd_xHg$ (11%)|Cd^{++}; E_0'.Cd(s)|Cd^{++}; E_0''

t	E_0	E_0'	E_0''	$E_0''(25)$
0	0.58151	0.3452	0.4006	0.4007[3]
5	.58039	.3465	.4010	.3986[18]
10	.57900	.3477	.4013	.3967[7]
15	.57755	.3491	.4016	.3982[8]
20	.57581	.3403	.4018	.3964[20]
25	.57300	.3515	.4020	.4026[14]
30	.57175	.3326	.4021	.4009[19]
35	.56955	.3539	.4020	.3960[7]
40	.56730	.3553	.4026	.4020[a]

[a] This investigation.

These results may be represented by the equation

$$E_0 = E_{0(25)} + \alpha_0(t - 25) + b_0(t - 25)^2 \qquad (13)$$

similar in form to equation (2). Numerical values of the constants of this equation are given at the bottom of Table I.

The function computed by equation (11) is certainly of the same form in dilute solutions as when computed from the observed electromotive forces. This gives us confidence that the method of extrapolation here employed is reasonable and that the values obtained for E_0 are a close approach to the true values. We note that the dissociation constant seems to decrease with increasing temperature but do not regard this determination as an accurate evaluation of this quantity.

Standard Potential of the Electrode: Cd(s)|Cd^{++}

The standard potential of the two-phase amalgam electrode of 11% total cadmium content, E_0', can be computed readily from the values of E_0 by subtracting the standard potentials of the hydrogen silver–silver chloride cell given by Harned and Ehlers[13] at the corresponding temperatures. The potentials thus obtained for the electrode $Cd-Cd_xHg$ (11%) / Cd^{++} are represented by E_0' and are given in the third column of Table II. Quintin[14] obtained 0.3491, 0.3521 and 0.3553 at 15, 25 and 35°, respectively, from an apparently identical cell by an application of the La Mer, Gronwall and Greiff[8] method. These values are in fair agreement with those obtained by us.

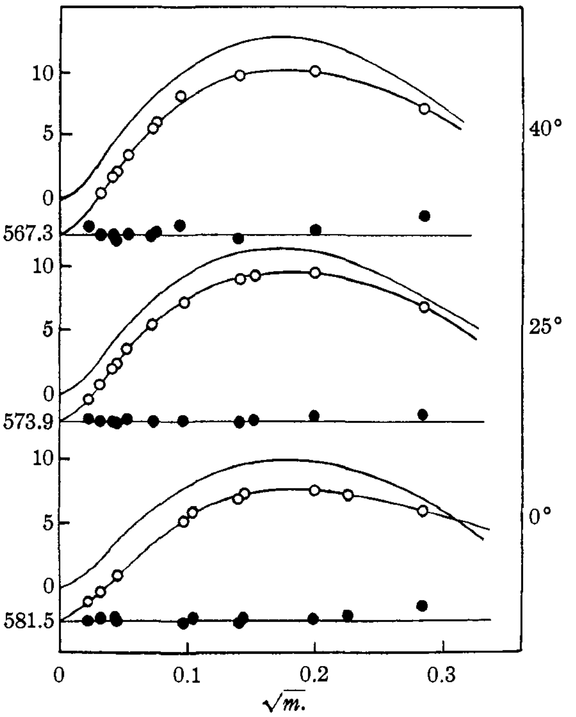

Fig. 1.—Extrapolation functions at 0, 25 and 40° (scale in millivolts, diameters of circles, 0.8 mv.): (1) Curves without points are theoretical according to Eq. (11). $E_H - E_0$ is plotted. (2) Circles represent plots of E_H according to Eq. (4). (3) Dots represent E_0 according to Eq. (12). (4) The dissociation constants were 0.010, 0.011 and 0.013 at 40, 25 and 0°, respectively.

Parks and La Mer[15] have measured the potential of cadmium amalgam of the same composition as that employed in the present investigation against cadmium. From their results and the values of E_0' in Table II, the values of the standard potential, E_0'', of the electrode Cd(s) / Cd^{++}, given in the fourth column of this table from 0 to 30° were computed. The values at 35 and 40° were computed from the results of Getman[16] for γ-cadmium. According to Cohen,[17] cadmium metal exists in three forms. Getman[16] measured cells of cadmium against cadmium amalgam over a time interval and found that only 10% main-

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[13] Harned and Ehlers, THIS JOURNAL, 55, 2179 (1933).

[14] Quintin, *Compt. rend.*, 200, 1754 (1935).

[15] Parks and La Mer, THIS JOURNAL, 56, 90 (1934).

[16] Getman, *ibid.*, 39, 1806 (1917).

[17] Cohen, "Physico-chemical Metamorphosis," McGraw-Hill Book, Co., Inc., New York, 1926, p. 43.

tained the original high value for the electromotive force which was due to γ-Cd, while the potentials of the other 90% dropped in value due to a change to α- or β-Cd. Parks and La Mer's results agreed with those obtained for γ-Cd by Getman, so that the values given by us in Table II are taken to refer to γ-Cd.

There have been many attempts to provide a sound extrapolation of the existing data on cadmium chloride at 25°. The last column of Table II contains values of E_0'' obtained by the investigators mentioned at the bottom of the table. The first four values were derived from Horsch's data, the fifth from Horsch's and Lucasse's and the remainder each used their own experimental results.

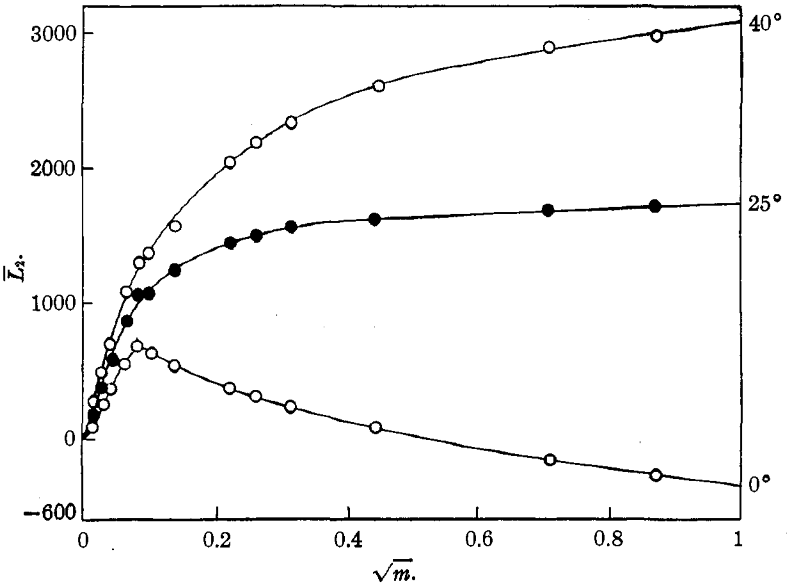

Fig. 2.—Relative partial molal heat content, $\bar{L}_2$. *versus* $\sqrt{m}$.

Brewster measured the potential of a cell with a liquid junction containing stick cadmium and calomel electrodes. German's second value was obtained from measurements of a cell containing cadmium in the form of a single crystal and a calomel electrode.

Some of the values have been changed. Horsch's[3] and Lewis and Randall's[18] values have been recalculated after correcting the silver chloride and calomel electrodes as indicated by the more recent values of the activity coefficient of hydrochloric acid. Quintin's silver chloride electrode was assumed to be the same as the type used by us. A correction of 0.0534 volt for the amalgam electrode used by Horsch was added to the value of E_0 obtained from his data, and one of 0.0505 volt to those obtained from amalgams of 11% total cadmium content. All results should refer to γ-Cd, although there remains some doubt regarding Getman's cell containing a single crystal. If this is α-Cd, a correction of 0.0031 volt should be added to Getman's second value.

The principal cause of the difference in values of these standard potentials is due to the methods of extrapolation. The first two determinations were made without the use of the limiting theoretical law of Debye and Hückel. This combined with giving too great weight to the determinations at extreme dilutions (<0.0004 M) tends to give results that are too low. Getman's extrapolation of Horsch's data and Brewster's[19] extrapolation of his own results were made by a plot suggested by equation (4). Again, the curve through the results in the concentration range available possesses a slope greater than the theoretical, and as a result intercepts the axis at zero molality at a value of E_0 which is too low. Getman's second value was computed by equation (3) from his results, and Horsch's activity coefficients. Activity coefficients computed from a low value of E_0 would be too large, which would make Getman's second value low also.

La Mer, Gronwall and Greiff could only fit the observed results with their equation upon the assumption of an apparent ionic diameter of 1 Å. Quintin's extrapolation seems reasonable, although the uncertainty is somewhat large because of the small number of points used. Scatchard and Tefft[20] used a function similar to equation (11) but made a rough application only and in our opinion placed too much weight on Horsch's results in very dilute solutions.

This critique of methods of extrapolation along with our experience indicates that the higher values of E_0'' ($\sim$ 0.402 volt) are more likely to be correct.

Activity Coefficient, Relative Partial Molal Heat Content and Specific Heat

The stoichiometric activity coefficient $\gamma_{\pm}$ may be computed from the values of E in Table I and

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[18] Lewis and Randall, "Thermodynamics," McGraw-Hill Book Co., Inc., New York, 1923, p. 360.

[19] Brewster, *Rec. trav. chim.*, **46**, 378 (1927).

[20] Scatchard and Tefft, THIS JOURNAL, **52**, 2272 (1930).

the values of E_0 in Table II by means of equation (3). Unfortunately, accurate freezing point and vapor pressure data have not been obtained for cadmium chloride solutions so that values of the activity coefficients derived from the different colligative properties are not available for comparison. Because of this, we have not tabulated activity coefficients.

The relative partial molal heat content, $\bar{L}_2$, has been computed from equations (2) and (13) by the method given by Harned and Thomas.[21] For a bi-univalent electrolyte, equation (17) of Harned and Thomas is

$$\bar{L}_2 = 2\alpha + 2\beta T^2 \qquad (14)$$

where the constants α and β may be computed from the constants of equations (2) and (13). Equation (14) is a necessary consequence of the quadratic temperature variation of E and E_0, and should only be applied to the temperature range (0 to 40°) in which the experimental results were found to conform closely to the quadratic relationship. In Table III, values of α and β are given at the concentrations designated. Values of $\bar{L}_2$ at 25° are recorded in the table and plots of this quantity at 0, 25 and 40° are shown in Fig. 2. In the last column of the table, values of the relative partial molal specific heat, $\bar{C}_p - \bar{C}_{p_0}$, at 25° computed from the equation

$$\bar{C}_p - \bar{C}_{p_0} = 4\beta T \qquad (15)$$

are also given. We have been unable to find accurate calorimetrically determined values of these quantities so that further confirmation or disproof of the accuracy of these results and calculations cannot be obtained at the present time.

TABLE III

$\bar{L}_2$, AND $(\bar{C}_p - \bar{C}_{p_0})$ IN CALORIES. CONSTANTS OF EQ. (14)

m	$-\alpha$	β	$\bar{L}_{2(298)}$	$(\bar{C}_p - \bar{C}_{p_0})_{298}$
0.0005	207	0.0035	186	4
.001	277	.0053	387	6
.002	392	.0076	566	9
.005	590	.0115	868	14
.007	710	.0141	1077	17
.01	885	.0160	1075	19
.02	1577	.0248	1254	30
.05	2566	.0364	1446	43
.07	2861	.0401	1505	48
.1	3232	.0449	1556	54
.2	3943	.0538	1634	64
.5	4946	.0652	1689	78
.7	5303	.0693	1708	83
1.0	5674	.0736	1720	88

Summary

1. Measurements of the cells Cd–Hg_xCd (11%) | $CdCl_2$ (m) | AgCl–Ag from 0 to 40° and at concentrations from 0.0005 to 1 M have been made.

2. The standard potential of the cell from 0 to 40° has been computed by a method which assumes incomplete dissociation of an intermediate ion, the dissociation constant of which was estimated to be 0.013, 0.011 and 0.010 at 0, 25 and 40° respectively.

3. The standard potential of the electrode: Cd_γ(s) | Cd^{++}, has been computed from 0 to 40°.

4. The relative partial molal heat content and specific heat of cadmium chloride in aqueous solution have been calculated.

NEW HAVEN, CONN.

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[21] Harned and Thomas. THIS JOURNAL **58**, 761 (1936).