

# SOME HEATS OF DILUTION AND RELATED THERMAL QUANTITIES OF AQUEOUS CADMIUM CHLORIDE, BROMIDE, AND IODIDE SOLUTIONS<sup>1</sup>

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Measurements of the heats of dilution of aqueous cadmium chloride, bromide, and iodide solutions at 15° and 25°C. are reported. The data are treated to obtain relative partial molal heat contents, heat capacities, and entropies. The results are discussed with reference to the Debye-Hückel limiting law in extremely dilute solutions and in terms of ion association in more concentrated solutions. Comparison is made with similar data obtained from E.M.F. measurements.

## I. INTRODUCTION

The heats of dilution of strong electrolytes have been measured precisely in many cases and have afforded significant tests of the limiting law of Debye and Hückel (3, 6, 20). Analytical treatment of the data, particularly by Young and his coworkers (24, 25, 26), has shown excellent agreements with the theory for sixteen salts of the alkali metals of the 1-1 and 1-2 valence types. Young and Seligmann (25) consider this agreement "to be the most impressive quantitative confirmation yet received by the Debye-Hückel limiting law." Similar treatment of the results for the heats of dilution of 2-2 salts (23; 25, footnote 19) has shown deviations from the limiting law to a greater extent than could be accounted for by experimental error. Recently, however, using a slight modification of the treatment of Young, which will be described later in this paper, we have been able to show (18) that there is strong indication that better agreement with the limiting law exists than previously reported for the heats of dilution of these salts. In the cases of the sulfates of calcium, magnesium, copper, zinc, and cadmium, approach to the limiting law first becomes evident at concentrations below 0.001 *m*.

Although values for the relative partial molal heat contents and related quantities have been obtained for a number of weaker electrolytes by measurements with suitable cells, there is a lack of precise calorimetric measurements for these salts. It was with the purpose of extending our knowledge of the thermochemical properties of dilute aqueous solutions of such salts that these measurements were undertaken.

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## II. APPARATUS AND METHODS

The apparatus and method for determining heats of dilution have been adequately described by Lange and Robinson and their coworkers (4, 8, 14, 15, 22). The present experiments were performed using a Lange-type adiabatic differential calorimeter in which the temperature was measured by means of two 665 junction iron-constantan thermels connected in parallel. By observing the deflection of a Leeds and Northrup HS galvanometer connected directly to these thermels, a temperature change of  $10^{-7}$  degree could be detected, although, for most measurements, the electrical resistance of the circuit was so arranged as to limit the sensitivity to approximately 1 microdegree per millimeter deflection.

The calorimeter was identical with that used by Wallace and Robinson (22), with the exception of a few minor details.

Because of the susceptibility of iodide ion to atmospheric oxidation, an oxygen-free system was thought desirable. Oxygen-free water was prepared by boiling freshly distilled water and storing it under an atmosphere of commercial tank nitrogen until used. This "oxygen-free" water was used for the preparation of all cadmium iodide solutions. This same water was used as the dilution water in the calorimeter for all the measurements on cadmium iodide. Suitable precautions were taken to prevent the solution of atmospheric oxygen during the process of filling the calorimeter, and the various entrances to the system were blocked by oil traps to maintain the isolation of the calorimeter contents during the subsequent course of the experiment.

Agreement between results of experiments in which atmospheric oxygen was eliminated and those in which no particular precautions were exercised was taken as evidence that chloride and bromide solutions are not appreciably affected by atmospheric oxygen. Hence the experiments on the chloride and bromide solutions were performed without any attempt to exclude oxygen.

After a few experiments were performed using cadmium iodide solutions, it became evident that surface adsorption was making a small but appreciable contribution to the measured heats. Such effects were rendered inappreciable by coating the calorimeter walls with paraffin, and a suitable revision of the previously accumulated data was made.

The right-hand and left-hand pipets have volumes of 6.755 and  $6.782 \pm 0.004$  ml., respectively. The right-hand and left-hand calorimeters contain 1000 and  $1004 \pm 1$  ml., respectively.

The cadmium iodide and cadmium chloride were Mallinckrodt products of analytical reagent grade, and were used without further purification. The cadmium bromide was a Merck C.P. reagent, and was recrystallized before use. Stock solutions of these substances were made, the halogen contents of which were determined to one or two parts per thousand by titration with a standard silver nitrate solution, using dichlorofluorescein as an indicator. Solutions used in the experiments were prepared by dilution of the stock solutions, using calibrated volumetric glassware.

All solutions were made up by volume and then converted to a weight basis with the aid of densities obtained from the *International Critical Tables*.

## III. TREATMENT OF RESULTS

A. *Experimental heats of dilution*

The scheme of calculation to be followed for these salts is, in general, the same as that employed by Wallace and Robinson for sodium sulfate solutions (22).

For each initial concentration of salt two types of dilution were performed. A small volume, about 7 ml., of salt solution was diluted with about a liter of water and the heat effect ( $q_1$ ) accompanying the dilution was measured. In the second type of dilution the diluent was the dilute solution produced by the first type of dilution. The heat of this second type of dilution may be called  $q_2$ . From these data two heats of dilution may be computed:

$$\Delta H_{c_1 \rightarrow c_2} = q_1/n \quad \text{and} \quad \Delta H_{c_3 \rightarrow c_2} = 0.5017(q_1 - q_2)/n$$

where  $c_1$  is the initial concentration and  $c_2$  and  $c_3$  are the final concentrations after the first and second types of dilution, respectively. The  $\Delta H$ 's are the heats of dilution per mole of salt for the concentration change indicated.  $n$  is the number of moles that was actually diluted, and 0.5017 is a numerical factor arising from the particular volumes of pipets and calorimeters used.<sup>3</sup>

$\Delta H_{c_1 \rightarrow c_2}$  corresponds to a dilution of about 148-fold and will be designated hereafter as a long chord.  $\Delta H_{c_3 \rightarrow c_2}$  corresponds to a dilution of about twofold and will be designated as a short chord. These short chords are in the very dilute range where direct chords are difficult, if not impossible, to obtain. They are particularly important for the practical purpose of extrapolation to infinite dilution and for comparison with the limiting law.

To derive the equation as given above, one considers  $q_2$  as consisting of heats of dilution of  $n$  moles of solute from  $c_1$  to  $c_3$  and  $n(1 - \delta)$  moles of solute from  $c_2$  to  $c_3$ . The quantity  $\delta$  (= volume of pipet  $\div$  volume of calorimeter) enters as a result of the procedure followed when using a Lange-type calorimeter (14). Before filling the pipet for making the second dilution it must be emptied of its contents,—namely, the solution remaining after the first dilution. This removes  $n\delta$  moles of solute, so there remains  $n(1 - \delta)$  moles of solute. Then,

$$\begin{aligned} q_2 &= n\Delta H_{c_1 \rightarrow c_3} + n(1 - \delta)\Delta H_{c_2 \rightarrow c_3} \\ &= n\Delta H_{c_1 \rightarrow c_3} - n(1 - \delta)\Delta H_{c_3 \rightarrow c_2} \end{aligned}$$

Also

$$\Delta H_{c_1 \rightarrow c_2} = \Delta H_{c_1 \rightarrow c_3} + \Delta H_{c_3 \rightarrow c_2}$$

from which

$$q_2 = n\Delta H_{c_1 \rightarrow c_2} - n(2 - \delta)\Delta H_{c_3 \rightarrow c_2}$$

<sup>3</sup> This procedure is slightly different from that followed by Wallace and Robinson (22). They calculated  $\Delta H_{c_1 \rightarrow c_2}$  and  $\Delta H_{c_1 \rightarrow c_3}$  and then obtained  $\Delta H_{c_3 \rightarrow c_2}$  as the difference of these two quantities. This cumbersome method of calculation, while being numerically correct, magnifies excessively the transmission of errors in  $q_1$  and  $q_2$  to  $\Delta H_{c_3 \rightarrow c_2}$ .

TABLE I  
Experimental heats of dilution

INITIAL CONCENTRATION m%	FINAL CONCENTRATION m%	AT 25°C.		AT 15°C.	
		q	$\Delta H$	q	$\Delta H$
Cadmium chloride					
	<i>moles per kilogram of water</i>	<i>calories</i>	<i>calories per mole of salt</i>	<i>calories</i>	<i>calories per mole of salt</i>
0.2005	0.001348	-1.236 ± 0.006	-914 ± 4 (2)*	-0.825 ± 0.010	-610 ± 7 (4)*
0.1005	0.0006768	-0.551 ± 0.002	-812 ± 3 (3)	-0.3904 ± 0.0017	-575 ± 3 (2)
0.05033	0.0003397	-0.2524 ± 0.0008	-741 ± 2 (4)	-0.1766 ± 0.0023	-518 ± 7 (2)
0.02525	0.0001703	-0.1132 ± 0.0021	-662 ± 12 (3)	-0.0748 ± 0.0011	-438 ± 6 (2)
0.01265	0.0000855	-0.0456 ± 0.0003	-532 ± 4 (4)	-0.0294 ± 0.0003	-343 ± 3 (2)
0.002688	0.001348	-0.235 ± 0.012	-88 ± 4 (2)	-0.147 ± 0.000	-55 ± 0 (3)
0.001348	0.0006768	-0.078 ± 0.001	-58 ± 1 (2)	-0.0594 ± 0.0005	-44 ± 0.4 (2)
0.0006768	0.0003397	-0.0301 ± 0.0008	-44 ± 1 (4)	-0.0226 ± 0.0006	-33 ± 0.9 (2)
0.0003397	0.0001703	-0.0073 ± 0.0012	-21 ± 3 (3)	-0.0062 ± 0.0002	-18 ± 0.6 (2)
0.0001703	0.0000855	-0.0037 ± 0.0006	-22 ± 4 (4)	-0.0006 ± 0.0002	-2.5 ± 0.8 (2)
Cadmium bromide					
		<i>calories</i>	<i>calories per mole of salt</i>	<i>calories</i>	<i>calories per mole of salt</i>
0.7916	0.005363	-0.166 ± 0.004	-30.9 ± 0.7 (3)	+1.242 ± 0.008	+461 ± 3 (2)
0.4012	0.002690	-0.009 ± 0.003	-3.3 ± 1.1 (2)	0.642 ± 0.006	475 ± 4 (2)
0.2009	0.001350	+0.0753 ± 0.0000	+55.7 ± 0.0 (2)	0.3160 ± 0.0002	466 ± 0 (2)
0.1006	0.0006775	0.0736 ± 0.0004	108.4 ± 0.6 (3)	0.1523 ± 0.0008	477 ± 2 (2)
0.05043	0.0003400	0.0449 ± 0.0003	131.8 ± 0.6 (3)	0.0686 ± 0.0003	402 ± 2 (2)
0.02527	0.0001705	0.0230 ± 0.0001	134.6 ± 0.6 (2)	0.0286 ± 0.0002	333 ± 2 (2)
0.01266	0.0000856	0.00943 ± 0.00006	110.0 ± 0.7 (2)		
0.01069	0.005363	0.306 ± 0.008	28.6 ± 0.7 (3)	0.414 ± 0.002	77.1 ± 0.4 (2)
0.005363	0.002690	0.1532 ± 0.0020	28.5 ± 0.4 (2)	0.181 ± 0.003	67.3 ± 1.1 (2)
0.002690	0.001350	0.0634 ± 0.0008	23.5 ± 0.3 (2)	0.0607 ± 0.0012	44.8 ± 0.9 (2)
0.001350	0.0006775	0.0186 ± 0.0003	13.7 ± 0.2 (2)	0.0169 ± 0.0002	24.9 ± 0.3 (2)
0.0006775	0.0003400	0.0031 ± 0.0003	4.6 ± 0.5 (3)	0.0062 ± 0.0002	18.2 ± 0.6 (2)
0.0003400	0.0001705	0.0011 ± 0.0003	3.2 ± 0.9 (2)	0.0007 ± 0.0000	4.1 ± 0.0 (2)
0.0001705	0.0000856	0.00028 ± 0.00004	1.6 ± 0.2 (2)		

Cadmium iodide

0.1008	0.0006775	1.517	± 0.002	2235	± 3 (2)	1.957 ± 0.004	2883	± 6 (3)
0.05043	0.0003400	0.7112	± 0.0002	2088	± 1 (2)	0.919 ± 0.003	2697	± 9 (2)
0.02530	0.0001705	0.3056	± 0.0015	1789	± 9 (6)	0.4008 ± 0.0014	2345	± 8 (2)
0.01268	0.0008557	0.1286	± 0.0008	1500	± 9 (4)	0.1675 ± 0.0005	1954	± 6 (4)
0.006356	0.00004264	0.0513	± 0.0003	1192	± 6 (4)	0.0699 ± 0.0002	1626	± 5 (2)
0.003190	0.00002155	0.0206	± 0.0003	954	± 7 (4)	0.0264 ± 0.0005	1223	± 22 (2)
0.001350	0.0006775	0.296	± 0.007	216	± 5 (2)	0.398 ± 0.003	295	± 4 (2)
0.0006775	0.0003400	0.1105	± 0.0001	163	± 0 (2)	0.147 ± 0.001	217	± 1 (2)
0.0003400	0.0001705	0.0352	± 0.0011	104	± 3 (6)	0.0476 ± 0.0007	139	± 2 (2)
0.0001705	0.0008557	0.0092	± 0.0004	54	± 2 (4)	0.0152 ± 0.0008	89	± 5 (2)
0.00008557	0.00004264	0.00265	± 0.00005	31	± 1 (4)	0.0050 ± 0.0002	58	± 2 (2)
0.00004264	0.00002155	0.0014	± 0.0002	33	± 5 (4)	0.0008 ± 0.0001	19	± 2 (2)

\* The figures in parentheses indicate the number of runs.

but

$$n\Delta H_{c_1 \rightarrow c_2} = q_1$$

so

$$\Delta H_{c_3 \rightarrow c_2} = (q_1 - q_2)/n(2 - \delta)$$

which, after substituting the proper numerical value for  $\delta$ , gives

$$\Delta H_{c_3 \rightarrow c_2} = 0.5017(q_1 - q_2)/n$$

In table 1 the data leading to the calculation of the heats of dilution are summarized. The first two columns give the initial and final concentrations of a dilution, respectively. The remainder of the table gives the experimental heat effects and heats of dilution per mole of salt at the two temperatures studied.

Data for the calculation of the short chords have been entered in table 1 just as if they were performed directly. For the short chords  $c_3$  and  $c_2$  are given in

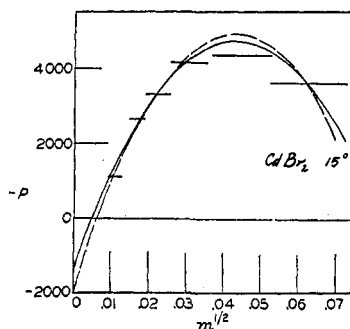


FIG. 1. Plot of the short chords (average value of  $d\Phi L_2/dm^{1/2}$ ) for aqueous cadmium bromide solutions at  $15^\circ\text{C}$ . as a function of the square root of the concentration. Solid line calculated from equation 1; broken line calculated from equation 6.

the columns headed  $m_1$  and  $m_2$ , respectively, while  $q_1 - q_2$  has been tabulated under the column headed  $q$ .

### B. The extrapolation

For extrapolation to infinite dilution from the lowest measured final concentration, we have used a modification of the method of Young (24, 25). As an example we use the data for cadmium bromide at  $15^\circ\text{C}$ . Figure 1 shows a plot of the short chords derived from the heats of dilution in the very dilute concentration range, obtained in the manner just described. Each of these chords represents the average value of the derivative of the apparent molal heat content with respect to the square root of the concentration in the small concentration range defined by the length of the chords. A smooth curve through these chords may be determined by a graphical or analytical procedure. The intercept of this curve on the ordinate axis gives the experimental limiting slope, and the area under the curve to a concentration  $m$  gives the relative apparent molal heat content, or its negative the integral heat of dilution at that concentration.

The heats of dilution of cadmium bromide at  $15^\circ\text{C}$ . were of such a sign and

magnitude as to be in a range wherein the Lange-type calorimeter operates most successfully. For this reason these data are particularly precise (compared to the other five cases) and hence were chosen for use in the analytical treatment. For representation of these data a quadratic equation in  $m^{1/2}$  was chosen, and the constants were determined by the method of least squares. The equation so obtained is

$$S = 1367 - 280,490m^{1/2} + 3,209,580m \quad (1)$$

where  $S = d\Phi L_2/dm^{1/2}$ .

From equation 1 the limiting slope for cadmium bromide at 15°C. is seen to be 1367. It is obvious that, because of the great curvature exhibited by the plot in figure 1, the limiting slope as evaluated cannot be of very great precision. An estimate of the precision of the limiting slope can be made fairly rigorously by means of the familiar equation for the propagation of precision indices (17). If we have

$$U = U(x_1, x_2, x_3 \cdots x_n) \quad (2)$$

where  $x_1, x_2, x_3$ , etc. are measured quantities having probable errors  $p_{x_1}, p_{x_2}, p_{x_3}$ , etc., then

$$p_U = \sqrt{\sum_i p_{x_i}^2 (\partial U / \partial x_i)^2} \quad (3)$$

where  $p_U$  is the probable error of the derived quantity  $U$ .

In the application of the method of least squares the constants which are being sought are expressible as explicit functions of the measured quantities. In this particular case

$$S^0 = S^0(\Delta H_1, \Delta H_2 \cdots \Delta H_n, m_1, m_2 \cdots m_n) \quad (4)$$

where  $S^0$  is the limiting slope,  $\Delta H_1, \Delta H_2$ , etc. are the various measured heats of dilution, and  $m_1, m_2$ , etc. are the concentrations. Equation 3 may be used to evaluate the probable error of  $S^0$  in terms of the probable errors in the heats and concentrations. Making the reasonable assumption that the probable errors of the concentrations are negligibly small compared to errors in the heats of dilution,

$$p_{S^0} = \sqrt{\sum_i p_{\Delta H_i} (\partial S^0 / \partial \Delta H_i)^2} \quad (5)$$

With the aid of probable errors listed in column 6 of table 1,  $p_{S^0}$  is found to be  $\pm 1020$  or  $S^0 = 1367 \pm 1020$ . The Debye-Hückel limiting slope for a 2-1 salt at 15°C. is 2044. Hence, the data presented in this paper seem to indicate that cadmium bromide *does* obey the limiting law within the limit of error of the experiments, although such obedience is not apparent at concentrations larger than 0.0001  $m$ .

It is a matter of some interest to derive an equation of the same type as equation 1, using the theoretical value of  $S^0$ . Such a treatment gives

$$S = 2044 - 325,340m^{1/2} + 3,775,800m \quad (6)$$

Equations 1 and 6 when integrated with respect to  $m^{1/2}$  give, respectively,

$$\Phi L_2 = 1367m^{1/2} - 140,250m + 1,069,870m^{3/2} \quad (7)$$

$$\Phi L_2 = 2044m^{1/2} - 162,670m + 1,258,600m^{3/2} \quad (8)$$

Values for  $\Phi L_2$  computed from these equations may be used to evaluate heats of dilution for the same concentrations as were used experimentally. The results of such calculations are presented in table 2. The deviations listed in columns 6 and 7 of table 2 show that an equation containing the theoretical limiting slope is almost as successful in reproducing the measured heats of dilution as is an equation in which the initial slope determined by the method of least squares is used; particularly is this true for the lowest concentrations studied.

The deviations listed in column 6 of table 2 are seen to be for most cases larger than the probable errors assigned to the experimental heats of dilution. This is not surprising, since the latter quantities do not include the systematic

TABLE 2  
Comparison of measured and calculated heats of dilution of aqueous solutions of cadmium bromide at 15°C.

$m_i$	$m_f$	$\Delta H$			DEVIATIONS ( $\Delta H_{\text{calcd.}} - \Delta H_{\text{exptl.}}$ )	
		Experimental	Equation 7	Equation 8	Equation 7	Equation 8
<i>moles of salt per kilogram of water</i>		<i>calories per mole of salt</i>			<i>calories per mole of salt</i>	
0.005363	0.002690	77.1 ± 0.4	74.8	72.2	-2.3	-4.9
0.002690	0.001350	67.3 ± 1.1	71.2	74.1	+3.9	+6.8
0.001350	0.0006775	44.8 ± 0.9	45.5	47.3	+0.7	+2.5
0.0006775	0.0003400	24.9 ± 0.3	24.7	25.1	-0.2	+0.2
0.0003400	0.0001705	18.2 ± 0.6	12.2	11.5	-6.0	-6.7
0.0001705	0.0000856	4.1 ± 0.0	5.0	4.2	+0.9	+0.1

errors inherent in such measurements, whereas the deviations do to a certain extent take account of this type of error. Hence, the deviations are more likely to be a proper estimate of the accuracy of these measurements than are the probable errors given.

It might be pointed out that in the treatment given above no assumptions as to incomplete dissociation are involved. The E.M.F. data for these salts have customarily been extrapolated to infinite dilution with the aid of the Gronwall, La Mer, and Sandved (7) extension of the Debye-Hückel theory or by assumption of some plausible association equilibrium.

Qualitatively, all three salts at both temperatures indicate an approach to the limiting law similar to that revealed in figure 1; the precision for the other cases seemed insufficiently high to justify an attempt at quantitative comparison with theory.

Equation 7 may be used to compute values for the relative apparent molal heat contents of cadmium bromide solutions at 15°C. for  $m \leq 0.005$ . For the other five cases included in this investigation, graphical extrapolations of the short chords



were carried out, and estimates of the uncertainties introduced into the  $\Phi L_2$  values by the extrapolations were made from a comparison of the  $\Phi L_2$ 's so obtained and those yielded by an extrapolation to the theoretical limiting slope.  $\Phi L_2$  values for the higher concentrations were obtained by addition of the measured

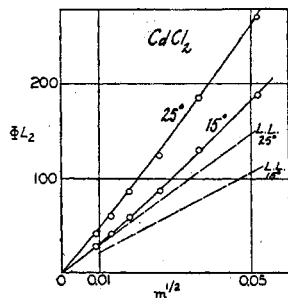


FIG. 2

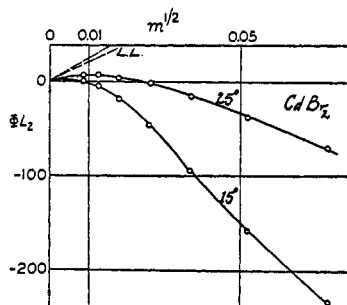


FIG. 3

FIG. 2.  $\Phi L_2$  (calories per mole of cadmium chloride) vs.  $m^{1/2}$  at 15° and 25°C. for aqueous cadmium chloride solutions at extreme dilutions. Dashed lines represent the Debye-Hückel limiting law for the two temperatures.

FIG. 3.  $\Phi L_2$  (calories per mole of cadmium bromide) vs.  $m^{1/2}$  at 15° and 25°C. for aqueous cadmium bromide solutions at extreme dilutions. Dashed lines represent the Debye-Hückel limiting law for the two temperatures.

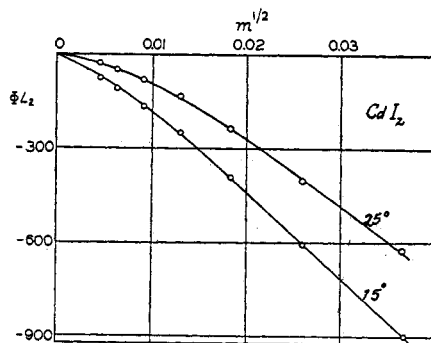


FIG. 4

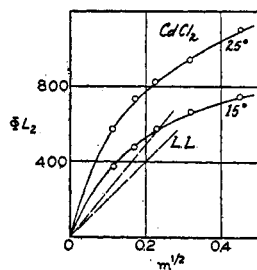


FIG. 5

FIG. 4.  $\Phi L_2$  (calories per mole of cadmium iodide) vs.  $m^{1/2}$  at 15° and 25°C. for aqueous cadmium iodide solutions at extreme dilutions.

FIG. 5.  $\Phi L_2$  (calories per mole of cadmium chloride) vs.  $m^{1/2}$  at 15° and 25°C. for aqueous cadmium chloride solutions. Dashed lines represent the Debye-Hückel limiting law for the two temperatures.

heats of dilution to the  $\Phi L_2$  values for the various final concentrations. The resulting  $\Phi L_2$ 's are represented graphically in figures 2, 3, 4, 5, 6, and 7.

Values for the relative apparent molal heat contents at several rounded concentrations are displayed in table 3. We estimate the uncertainty of the calorimetric  $\Phi L_2$ 's to be for cadmium chloride 10 calories per mole, for cadmium

bromide 5 calories per mole, and for cadmium iodide 15 calories per mole, of which the greater portion is due to the extrapolation.

*C. Evaluation of the relative partial molal heat contents, heat capacities, and entropies*

Using mechanically determined slopes obtained from large-scale plots of  $\Phi L_2$  versus  $m^{1/2}$ , values for  $\bar{L}_2$ , the relative partial molal heat content, were calculated by conventional methods (19). These values are compared with the results of E.M.F. studies in figures 8 to 10. Also included in table 3 are values for  $\bar{L}_2$  at several rounded concentrations.

Figure 8 shows that the  $\bar{L}_2$ 's for cadmium chloride (11) are in considerable disagreement below 0.01  $m$ . Above this concentration there is a constant difference of approximately 375 calories. The estimated uncertainties in the calorimetric  $\bar{L}_2$ 's are 15 calories per mole. According to Harned (12, 13) a precision

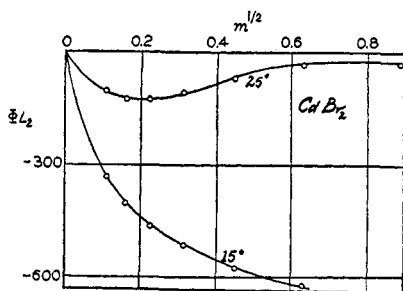


FIG. 6

FIG. 6.  $\Phi L_2$  (calories per mole of cadmium bromide) vs.  $m^{1/2}$  at 15° and 25°C. for aqueous cadmium bromide solutions.

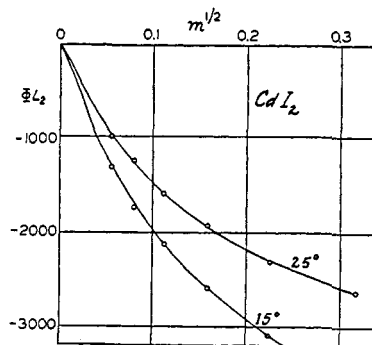


FIG. 7

FIG. 7.  $\Phi L_2$  (calories per mole of cadmium iodide) vs.  $m^{1/2}$  at 15° and 25°C. for aqueous cadmium iodide solutions.

of 30 to 50 calories per mole is about as good as can be expected for the E.M.F.  $\bar{L}_2$ 's, so that if we accept this as a proper estimate of the reliability of the  $\bar{L}_2$ 's for cadmium chloride (Harned and Fitzgerald do not give an estimate of the precision of their results), the above-mentioned discrepancies are considerably outside the limit of error of the two methods. Harned (10) has indicated the superiority of the calorimetric method for determining heat contents and has pointed out that if "electromotive forces yield results which agree closely with those determined calorimetrically, we have further evidence of their (the electromotive methods') fundamental validity." For some other cases (22) in which disagreement is similar in nature to the above-mentioned, the constant error has been attributed to difficulties in a proper extrapolation of the E.M.F. data and the behavior at low concentrations thought to imply a concentration region too dilute for proper operation of the cells. It is likely that a similar explanation is appropriate here.

Figure 9 shows that the  $\bar{L}_2$ 's for cadmium bromide (1) are, at high concentrations, in agreement within the limit of error of the two methods. However, below 0.01 *m* the discrepancies are larger than could be accounted for on the basis of the uncertainties assigned to the calorimetric  $\bar{L}_2$ 's (5 calories per mole)

TABLE 3

*Relative apparent and relative partial molal heat contents of aqueous cadmium halide solutions*

<i>m</i>	$\Phi L_2$		$\bar{L}_2$	
	25°C.	15°C.	25°C.	15°C.
Cadmium chloride				
<i>moles per kilogram of water</i>	<i>calories per mole of salt</i>		<i>calories per mole of salt</i>	
0.0001	45	31	67	47
0.0005	105	74	157	112
0.001	152	107	232	162
0.005	411	247	634	362
0.01	563	338	759	472
0.05	833	576	993	702
0.1	948	660	1134	778
0.2	1095	740	1323	860
Cadmium bromide				
0.0001	6.9	0.3	5.9	-4.0
0.0005	1.4	-32.4	-7.2	-74.3
0.001	-6.8	-68.6	-23.0	-134
0.005	-64.1	-228	-107.8	-343
0.01	-94.5	-302	-131.4	-414
0.05	-138.0	-462	-127.5	-540
0.1	-110.2	-513	-70.1	-591
0.2	-72.8	-569	-8.6	-639
0.4	-35.0	-619	-5.0	-686
0.8	-36.0		-71.2	
Cadmium iodide				
0.0001	-89	-179	-157	-287
0.0005	-323	-499	-564	-819
0.001	-514	-747	-828	-1148
0.005	-1147	-1556	-1587	-2155
0.01	-1463	-1990	-1941	-2622
0.05	-2305	-3058	-2789	-3700
0.1	-2636	-3430	-3108	-4074

and may indicate a certain amount of unreliability in the behavior of cadmium bromide cells below 0.01 *m*.

Figure 10 shows the  $\bar{L}_2$ 's for cadmium iodide (2) solutions. Here again, at high concentrations there seems to be a constant error which is larger than could be accounted for by the uncertainties in the calorimetric method (about 20

calories per mole) and suggests the possibility of an improper extrapolation of the E.M.F. data.

Average values for the relative partial molal heat capacities of the solutes,  $\bar{C}_{p_2} - \bar{C}_{p_2}^0$ , between 15°C. and 25°C., are shown in figure 11 and compared with the results of E.M.F. measurements.

These curves reveal a poorer agreement than has heretofore been obtained for strong electrolytes. We estimate the calorimetric heat capacities to be in error by not more than 3 to 4 calories per degree. Since the electrometric values

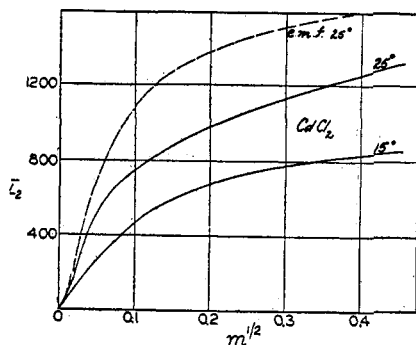


FIG. 8

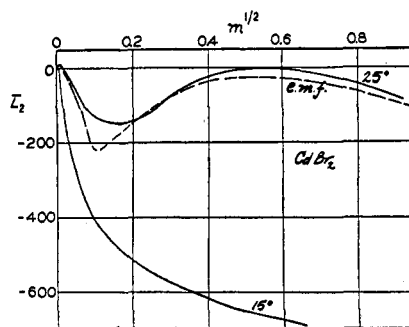


FIG. 9

FIG. 8.  $\bar{L}_2$  (calories per mole of cadmium chloride) vs.  $m^{1/2}$  at 15° and 25°C. Dashed curve shows E.M.F. results of Harned and Fitzgerald (11) at 25°C.

FIG. 9.  $\bar{L}_2$  (calories per mole of cadmium bromide) vs.  $m^{1/2}$  at 15° and 25°C. Dashed curve shows the E.M.F. results of Bates (1) at 25°C.

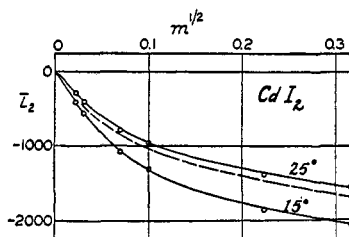


FIG. 10.  $\bar{L}_2$  (calories per mole of cadmium iodide) vs.  $m^{1/2}$  at 15° and 25°C. Dashed curve shows the E.M.F. results of Bates (2) at 25°C.

depend on the second derivative of E.M.F. with temperature, great precision for them is not to be expected. However, the deviations, especially at high concentrations, appear to be greater than could be accounted for by the combined uncertainties of the two determinations and hence imply the existence of some undetermined systematic errors in one or both types of measurements.

We have also computed values for  $\bar{S}_2 - \bar{S}_2^0$ , the relative partial molal entropies of the solutes, employing activity coefficient values obtained by Harned, Bates, and others (1, 2, 11) from cell measurements. The curves shown in figure 12 represent only the non-ideal part of the entropies; they do not include

the ideal entropy of mixing and thus go to a zero value at infinite dilution instead of to infinity. Also included in figure 12 is the non-ideal entropy for calcium chloride, calculated using activity coefficients from the E.M.F. measurements of Scatchard and Tefft (21) and  $\bar{L}_2$  values from the heat of dilution data of Lange and Streeck (16). A comparison of calcium chloride and cadmium chloride seems interesting, since the crystal radii of the two cations are nearly the same and therefore, presumably, at least at infinite dilution, their effect on the polarization of surrounding water molecules should be nearly equal.

#### IV. DISCUSSION OF RESULTS

The abnormalities of solutions of the cadmium halides have long been a subject of interest (see reference 1, footnote 3, and reference 2, footnotes 2 to 6).

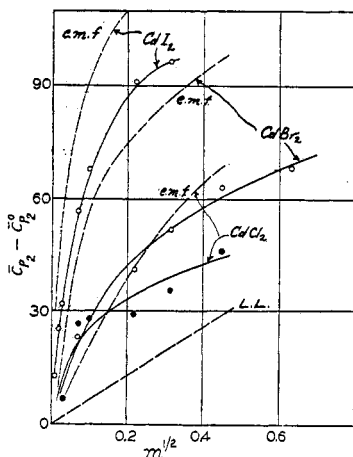


FIG. 11

FIG. 11.  $\bar{C}_{p_2} - \bar{C}_{p_2}^0$  (calories per mole per degree) vs.  $m^{1/2}$  for aqueous cadmium halide solutions and E.M.F. results (1, 2, 11).

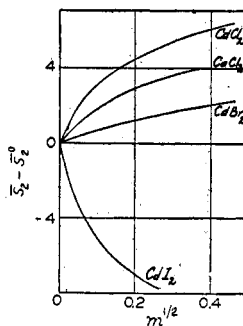


FIG. 12

FIG. 12.  $\bar{S}_2 - \bar{S}_2^0$  (calories per mole per degree) vs.  $m^{1/2}$  for aqueous solutions of cadmium halides and calcium chloride at 25°C.

All indications point to the existence of ion association in these solutions, although the nature and concentrations of the complex species are in general unknown. The thermochemical data presented in this paper seem to confirm the general suspicions harbored concerning these solutions.

Compared with other electrolytes of the same valence type, the  $\Phi L_2$  values are unusually negative for cadmium bromide and cadmium iodide and unusually positive for cadmium chloride. Since it has been shown, independent of any assumptions regarding ion association, that there is a fair indication of approach to the limiting law for these three salts, it seems plausible to attribute at least a part of the abnormalities to a heat of dissociation as a concentrated solution is diluted. This would mean that the heat of dissociation is positive for cadmium bromide and particularly so for cadmium iodide and negative for cadmium chloride.

The relative partial molal heat capacities are unusually high for these salts, particularly when compared with the values for a strong electrolyte of the same valence type (9, 22). The shape of the curves is also unusual. After an initial steep rise with  $m^{1/2}$ , the curves flatten out and become concave toward the  $m^{1/2}$  axis. It might be mentioned that the heat capacities of cadmium sulfate (4) show a similar trend. For most strong electrolytes the curves are approximately linear with  $m^{1/2}$  up to concentrations of several molal and do not differ greatly from the limiting law. The extra heat capacities of the cadmium halides could be interpreted as due to a heat absorbed by the association change which takes place as a solution is heated. The shape of the curves suggests a resemblance to the trend of  $d\alpha/dm$  with  $m$  ( $\alpha$  is the degree of dissociation), the steep portion of the curve corresponding to the concentration region wherein the degree of dissociation changes most rapidly with  $m$ . If this interpretation were correct, it would indicate the largest degree of association for cadmium iodide and the least for cadmium chloride. This is also the order indicated by the apparent heat contents.

Examination of the partial molal entropies of strong electrolyte solutions by Frank and Robinson (5) disclosed that for a given cation the order of  $\bar{S}_2 - \bar{S}_2^0$  is  $\text{Cl}^- > \text{Br}^- > \text{I}^-$  and all deviations from the limiting law are negative. Assuming complete dissociation for the alkali-metal halides, this order and a part of the deviations were interpreted as an extra orienting effect which an ion can exert on its water envelope. This extra orienting effect is due to the progressive weakening of the *total* water structure produced by ions unable to fit smoothly into this structure and the consequent enhanced ability of the ions to form a well-ordered *envelope* of water. Iodide ion effects the maximum disturbance of the water structure for the alkali halides. The same order is found for the entropies of the cadmium halides.

To consider the possible effects of association we compare the partial molal entropies of cadmium chloride and calcium chloride, the cations of which are of about the same size. Data are not available for a similar comparison of the other halides. From figure 12 we observe that the cadmium chloride entropies are more positive. This extra entropy could be considered, in terms of this discussion, as due principally to extra entropy returned to the water envelope when a pair of ions associates and releases some envelope water.

#### V. SUMMARY

Heats of dilution of aqueous cadmium chloride, bromide, and iodide have been studied at 15° and 25°C. over a concentration range extending from about 0.0001  $m$  (0.00002  $m$  for cadmium iodide) up to several tenths  $m$  (0.1  $m$  for cadmium iodide). Using the chord area method in the extremely dilute range, the measurements have been extrapolated to infinite dilution to obtain values for the relative apparent molal heat contents.

Relative partial molal heat contents, heat capacities, and entropies (non-ideal part) have been evaluated for the concentration range studied.

Qualitatively, approach to the limiting law is indicated for all cases studied.

The one case for which the precision in the extremely dilute range seemed sufficiently high to justify quantitative comparison with theory, *viz.*, that of cadmium bromide at 15°C., gave an experimental limiting slope of  $1367 \pm 1020$ , which agrees with the theoretical limiting slope (2044) within the limit of error.

Comparison of thermal properties of the solutions with the corresponding quantities derived from cell measurements reveals deviations which are in most cases larger than could be accounted for by the stated precisions of the measurements. This emphasizes the great difficulties involved in obtaining precise thermal data from cell measurements, particularly for weak electrolytes.

The thermal properties of the cadmium halide solutions are consistent with existing views regarding the presence of particles in the solutions other than the simple anions and cations. Accepting the suggestion that the slow approach of these salts to limiting behavior is to be attributed to incomplete dissociation, the conclusion is reached that dissociation decreases from the chloride to the bromide to the iodide.

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