35°, respectively, with which our values of 0.153 and 0.144, respectively, are to be compared.

Summary

The solubility of silver iodate in nitric acid solutions was measured at 25, 30 and 35°. These results, together with the results obtained previously for the solubility of silver iodate in potassium nitrate solutions, were used to calculate the thermodynamic constant of iodic acid at the three temperatures. Our value for the thermodynamic constant at 25° is in agreement with values given in the literature. Our values for 30 and 35° are in agreement with values extrapolated from the results derived from conductivity data.

PEIPING, CHINA RECEIVED OCTOBER 10, 1940

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, YALE UNIVERSITY]

The Thermodynamics of Bi-univalent Electrolytes. VI. Solutions of Cadmium Iodide from 5 to 40°

BY ROGER G. BATES[1]

Although many workers have found the abnormal behavior of cadmium iodide solutions a subject of interest,[2–6] a thermodynamic study over a range of temperature has never been made. In an earlier paper of this series,[6b] however, activity coefficients calculated from electromotive force measurements of cadmium amalgam–mercurous iodide cells at 25, 30 and 35° were reported. Whereas this range of temperature was not sufficiently large to warrant the calculation of thermodynamic quantities derived from the temperature coefficient, it appeared that the variation of electromotive force with temperature was essentially linear over a wide range of cadmium iodide concentration. The interesting implications of such a relationship made it seem worthwhile to study solutions of cadmium iodide over a wider range of temperature than that previously employed.

Electromotive force measurements of the cell

$$\text{Cd-Hg (2-phase)} \mid \text{CdI}_2\ (m) \mid \text{AgI-Ag} \qquad (1)$$

were made at intervals of 5° over the range, 5 to 40°, and at molalities of cadmium iodide ranging from 0.002 to 2. Activity coefficients, relative partial molal heat contents and relative partial molal specific heats of the solute have been evaluated. Between 0.05 and 2 molal the electromotive force of cell (1) was found to vary linearly with temperature, within the limits of error of the measurements. The relative partial molal specific heat is accordingly constant in this range.

Materials and Experimental Procedure

The mercury–mercurous iodide electrode used in the earlier investigation[6b] of cadmium iodide solutions has been shown[7] to give uncertain results when the iodide ion concentration is greater than *ca.* 0.02 *M*. Although the iodide ion concentration in cadmium iodide solutions is low, the silver–silver iodide electrode was chosen for the work. The solubility of silver iodide is small in iodide solutions containing up to 0.5 mole of iodide per liter.

The cadmium–silver iodide cell was found to be very satisfactory at molalities of cadmium iodide in excess of 0.005. The reproducibility fell off rapidly at molalities below 0.003. In general, the life of cells containing silver iodide electrodes was not as great as that of similar cells utilizing mercurous iodide electrodes,[8] and it was found necessary, for best results, to complete all measurements within thirty-six hours after the cells were made.

The slight acid reaction of cadmium iodide solutions (through hydrolysis) facilitates oxidative decomposition and makes exclusion of air essential. At no time was the presence of oxygen indicated by erratic potentials, by a dull amalgam surface or by a yellowing of the electrolyte

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(1) Sterling Fellow in Chemistry, 1937–1939; present address: National Bureau of Standards, Washington, D. C.

(2) Transference: Hittorf, *Pogg. Ann.*, **106**, 543 (1859); B. Redlich, *Z. physik. Chem.*, **37**, 673 (1901); Heym, *Ann. phys.*, **12**, 443 (1919).

(3) Conductance: West and Jones, *Am. Chem. J.*, **44**, 508 (1910); Van Rysselberghe, Grinnell and Carlson, THIS JOURNAL, **59**, 336 (1937).

(4) Partial molal volume: Cantelo and Phifer, *ibid.*, **55**, 1333 (1933); Gibson, *ibid.*, **59**, 1521 (1937).

(5) Complex ion equilibria: McBain, Van Rysselberghe and Squance, *J. Phys. Chem.*, **35**, 999 (1931); Riley and Gallafent, *J. Chem. Soc.*, 514 (1932); Bates and Vosburgh, THIS JOURNAL, **60**, 137 (1938).

(6) Activity coefficients: from cells without liquid junctions, (a) Getman, *J. Phys. Chem.*, **32**, 940 (1928); (b) Bates and Vosburgh, THIS JOURNAL, **59**, 1583 (1937); from freezing points of solutions, (c) Getman, *J. Phys. Chem.*, **33**, 1781 (1929); see also (d) Rosenfeld, "Landolt-Börnstein Tabellen," Julius Springer, Berlin, 1931, II, b, 1116; from isopiestic vapor pressure, (e) Robinson and Wilson, *Trans. Faraday Soc.*, **36**, 740 (1940).

(7) Vosburgh, Derr, Cooper and Bates, THIS JOURNAL, **61**, 2592 (1939).

(8) Taylor and Perrott, *ibid.*, **43**, 389 (1921), measured the temperature coefficient of cell (1) with saturated (2.4 *m*) cadmium iodide electrolyte. They encountered difficulty in obtaining good results and suggested the formation of a cadmium–silver complex as the cause. The author has observed the same erratic behavior of the saturated cell but has found no evidence of a similar effect with oxygen-free 2 *m* cadmium iodide.

with free iodine. The stock solutions were prepared with boiled conductivity water and were preserved under purified hydrogen in Pyrex flasks from which they could be expelled by hydrogen pressure as needed. Cell electrolytes were prepared by weight dilutions of these solutions with pure, oxygen-free water in flasks of similar design but of smaller size (1-liter capacity).

The cell vessels were of the type described previously,[6b] modified to permit the use of an amalgam vessel and the vacuum-hydrogen technique. A rack of six cells was employed.

With a dry silver–silver iodide electrode held in place in one arm by a rubber stopper, the cell vessel was evacuated and a portion of molten amalgam drawn into the other arm of the vessel through the ungreased stopcock of the amalgam flask. Dry hydrogen was admitted, followed by cell electrolyte in sufficient quantity to wash both electrodes and the inner surface of the vessel. Two portions of wash electrolyte were admitted and expelled by hydrogen pressure before the cell was completely filled.

Three cells were made for each molality. In general, these were allowed to remain at 25° overnight to attain their equilibrium values. After a lapse of about twelve hours the deviations of triplicate cells from the mean electromotive force were usually of the order of 0.05 to 0.1 mv. At the conclusion of each run the group of cells was brought back to 25°. Any significant difference between the initial and final readings was considered sufficient reason for rejecting the run as unsatisfactory. Each temperature coefficient run was completed within a period of six to nine hours.

The temperature of the water thermostat was controlled within ±0.03° at all temperatures. The thermometer was calibrated against a platinum resistance thermometer certified by the National Bureau of Standards. The standard cell was a saturated cell of low temperature coefficient kindly given to the author by Professor Warren C. Vosburgh.[9] It was checked frequently against a group of six laboratory standards certified by the National Bureau of Standards.

Cadmium Iodide.—Two stock solutions of cadmium iodide were used in preparing the cell electrolytes. The first was 0.1 *M* and was prepared from "Analytical Reagent" cadmium iodide that had been further purified by recrystallization from conductivity water with rapid drying in a vacuum desiccator. The second stock solution was about 2 *M* and was prepared from salt that had not been recrystallized. This grade of salt was shown by Dr. Ralph G. Van Name of this Laboratory to be free of lead. The ten most dilute electrolytes were prepared from the first stock solution.

Both stock solutions were analyzed by weighing the silver iodide formed by the addition of a slight excess of silver nitrate to acidified samples of solution.[10] The silver iodide was digested in the dark at 60° for twelve hours, filtered on sintered glass crucibles and dried to constant weight at 120°. Triplicate analyses agreed to 0.02%. Vacuum corrections were made on all weighings.

Cadmium Amalgam Electrodes.—An amalgam containing 10% of cadmium by weight is heterogeneous over the temperature range, 5 to 40°. Kahlbaum redistilled cadmium was dissolved in nine times its weight of thrice-distilled mercury with gentle heating and the resulting amalgam transferred to the amalgam vessel. The air was then pumped out and the vessel filled with pure, dry hydrogen. Shortly before an electrode was to be prepared the vessel was placed in an electric oven to melt the amalgam to homogeneity.

Silver–Silver Iodide Electrodes.—The silver iodide electrodes were always freshly made for each run a few hours before the cells were prepared. The thermal type of electrode prepared as described in an earlier paper of this series[11] was found to be most satisfactory. An intimate mixture of 10% silver iodide and 90% silver oxide was heated on spirals of platinum wire to 450–500° for about ten minutes to form an adherent, porous mass of silver and silver iodide.

Results

The electromotive forces of cell (1) recorded in the fifteen satisfactory runs are listed in Table I. At each molality the observed electromotive forces were fitted by a graphical method[12] to quadratic equations of the type

$$E_T = A + BT + CT^2 \qquad (2)$$

The average deviation, Δ, in millivolts[13] of observed values at the eight temperatures from those calculated by equation (2) is given in the last column of Table I. Large scale plots of A, B and C *versus* log m were made, and values of these constants at round molalities were read off. Inspection of the interpolated constants listed in Table II shows that the variation of electromotive force between 5 and 40° with temperature is linear above $m = 0.05$, within the error of the measurements.

The plot of E_{25} against log m was sigmoid in form. The inflection occurred at a molality approximately equal to 0.14.

Standard Potentials of Cell (1)

The equation

$$(E/3k) + \log m + (\log 4)/3 = (E^0/3k) - \log \gamma_{\pm} \qquad (3)$$

where k is written for 2.3026 $RT/2F$, relates the electromotive force, E, of cell (1) with its standard potential, E^0, the molality, m, and the stoichiometrical activity coefficient, $\gamma_{\pm}$, of the cadmium iodide electrolyte. Since $\gamma_{\pm}$ by definition becomes equal to unity at infinite dilution, the left-hand side of equation (3) approaches $E^0/3k$ as m

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(9) This cell was #754 described by Vosburgh, Guagenty and Clayton, THIS JOURNAL, **59**, 1256 (1937). Its electromotive force at 26° was 1.01839 v. The change of e. m. f. during the eight months of observation amounted to less than 0.01 mv.

(10) Hillebrand and Lundell, "Applied Inorganic Analysis," John Wiley, New York, N. Y., 1929, p. 591.

(11) Bates, THIS JOURNAL, **60**, 2983 (1938).

(12) The constants of the equation $E_t = E_{25} + b(t - 25) + c(t - 25)^2$ were first obtained and the transformation to the absolute temperature scale made by substituting $T = t + 273.2$.

(13) $\Delta = \Sigma|\Delta E|/8$.

TABLE I

ELECTROMOTIVE FORCES OF THE CELL

Cd–Hg (2-phase) | CdI_2 (m) | AgI–Ag

m	E_5	E_{10}	E_{15}	E_{20}	E_{25}	E_{30}	E_{35}	E_{40}	Δ
0.001224	0.43972	0.44381	0.44760	0.45136	0.45503	0.45885	0.46258	0.46586	0.09
.001925	.42796	.43171	.43529	.43860	.44202	.44539	.44875	.45199	.08
.003993	.40802	.41150	.41459	.41763	.42052	.42342	.42618	.42880	.05
.006407	.39707	.39999	.40278	.40538	.40805	.41073	.41334	.41575	.05
.007912	.39242	.39526	.39790	.40044	.40293	.40546	.40790	.41022	.04
.01250	.38291	.38553	.38785	.39002	.39214	.39439	.39649	.39883	.10
.02814	.36908	.37089	.37288	.37453	.37616	.37796	.37988	.38153	.06
.05128	.36080	.36234	.36396	.36540	.36690	.36829	.36984	.37140	.05
.07130	.35646	.35786	.35927	.36063	.36204	.36337	.36484	.36622	.02
.09542	.35313	.35448	.35577	.35701	.35820	.35949	.36082	.36217	.04
.14072	.34826	.34947	.35072	.35187	.35303	.35417	.35536	.35662	.03
.50281	.33303	.33389	.33478	.33569	.33655	.33735	.33830	.33922	.05
.83558	.32460	.32548	.32635	.32714	.32790	.32870	.32950	.33028	.03
1.4004	.31568	.31641	.31709	.31779	.31850	.31917	.31985	.32057	.02
2.0742	.30654	.30721	.30789	.30852	.30914	.30975	.31038	.31101	.02

becomes small. Precise experimental data at concentrations sufficiently low to make this expression useful for the calculation of standard potentials are unfortunately rarely obtained.

The standard potential may sometimes be obtained by substituting in equations similar to (3) empirical representations of log $\gamma_\pm$ which become more and more exact as m decreases. A plot of the "apparent E^0" against m will then often yield an unambiguous value of E^0 by a straight-line extrapolation to $m = 0$, in which limit the approximation to $\gamma_\pm$ becomes exact.

TABLE II

CONSTANTS OF EQUATION (2)

m	A	$B \times 10^5$	$C \times 10^6$
0.002	0.04496	198.41	−2.2
.005	.10592	151.12	−1.6
.007	.12761	135.10	−1.4
.01	.15961	112.50	−1.1
.02	.22229	68.62	−0.5
.05	.27742	30.10	0
.07	.28007	27.60	0
.1	.28145	25.60	0
.2	.28281	22.10	0
.5	.28298	18.00	0
.7	.28138	16.70	0
1.0	.27930	15.30	0
1.5	.27591	13.80	0
2.0	.27188	12.90	0

When the Debye–Hückel limiting law expression for a bi-univalent electrolyte

$$-\log \gamma_\pm = 1.02\sqrt{m} \qquad (4)$$

was substituted in equation (3) and the apparent E^0 values plotted as a function of molality, a curve exhibiting a rapid rise in the dilute solutions and a maximum at a molality of about 0.1 was obtained. The height of this hump (about 37 mv.) is evidence of the low degree of dissociation of the salt.[14,15]

Attempts at obtaining a satisfactory extrapolation function for evaluating standard potentials of cell (1) from the measured electromotive forces were uniformly unsuccessful. Extended forms of the Debye–Hückel equation were shown to give inadequate representations of log $\gamma_\pm$ for this abnormal electrolyte. Whereas a method was found for computing empirical corrections for first- and second-order ion interactions (CdI^+ and CdI_2 aggregates) which gave substantially straight-line plots of small slope below an ionic strength of 0.02, the accuracy of the extrapolation was in all cases considerably less than that desired.

Since extrapolation was impossible, it was necessary to evaluate E^0 for the cadmium amalgam–silver iodide cell by the combination of previously determined normal potentials for the two electrodes of which the cell was composed, according to the relationship

$$E^0 = E^0_{\text{Cd-Hg}} - E^0_{\text{AgI}} \qquad (5)$$

Recent values of the potential of the cadmium amalgam electrode over the desired range of temperature have been made available by the measurements of Harned and Fitzgerald[15a] and of Bates.[15b] Owen[16] has determined the normal potential of the silver iodide electrode over the range 5 to 40°, from measurements in potassium iodide

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

[15] The measurements of (a) Harned and Fitzgerald, *ibid.*, **58**, 2624 (1936), indicate a hump 11 mv. in height for cadmium chloride; the hump for cadmium bromide has a height of 17 mv.; (b) Bates, *ibid.*, **61**, 308 (1939).

[16] Owen, *ibid.*, **57**, 1526 (1935).

solutions buffered with borate. Measurements in acetate buffers from 10 to 40° also have been reported quite recently by Gould and Vosburgh.[17]

An examination of the literature, however, discloses evidence pointing to the conclusion that the silver iodide electrode has a different potential in cadmium iodide than in a potassium iodide solution of the same iodide content. Thus it has been found[7] from a study of the cell

$$\mathrm{Ag–AgI} \mid \mathrm{M}^{+n}, n\mathrm{I}^- \mid \mathrm{Hg_2I_2–Hg} \qquad (6)$$

with several different iodide electrolytes that (a) the use of cadmium iodide as the electrolyte yields a potential about 0.9 mv. lower than the equilibrium or "thermodynamic" value of 0.1112 v. at 25°, and that (b) an increase in the concentration of a completely dissociated iodide salt causes an increase in the cell potential by an amount which is dependent upon the iodide concentration and which may be as great as several millivolts. This second effect may be attributed to the difference in potassium iodide activity at the two electrodes resulting from the side reaction of mercurous iodide with iodide ion, thus lowering the iodide activity at the positive (mercurous iodide) electrode. The increase of electromotive force measures the free energy of transfer of iodide according to the equation

$$\Delta F_{\text{obsd.}} - \Delta F_{\text{equil.}} = -\mathrm{F}(E_{\text{obsd.}} - E_{\text{equil.}}) = RT\ln(a_{\mathrm{I_1}}/a_{\mathrm{I_2}}) \qquad (7)$$

The first effect appears to be virtually independent of the cadmium iodide concentration. When the potential of cell (6) was computed for thirteen different cadmium iodide molalities varying from 0.005 to 2 by combining the measurements of the cadmium–mercurous iodide cell[6b] with those of the cadmium–silver iodide cell presented in this paper no definite trend was to be noted. The average potential was 0.1103; the mean deviation of all results from this value was 0.4 mv. It is probable, then, that the cells containing mercurous iodide electrodes and those containing silver iodide electrodes are measuring the same quantity and that both are reversible to cadmium iodide.

The anomalous effect of cadmium iodide in lowering the electromotive force of cell (6) might be exerted upon either electrode. That it is not the mercury–mercurous iodide electrode that is responsible for the observed effect is shown by the results of Vosburgh[18] who found the same potential for the lead–mercurous iodide cell with cadmium iodide electrolyte as with potassium iodide.

Since the normal potential of the mercury–mercurous iodide electrode is known[19] to be 0.0405 at 25°, a value of 0.1508 may be assigned to the hypothetical cell

$$\mathrm{Ag–AgI} \mid \mathrm{Cd}^{++}, \mathrm{I}^- (a = 1), \mathrm{H}^+ (a = 1) \mid \mathrm{H_2} \qquad (8)$$

with a fair degree of certainty. From equation (5), then, E^0 is calculated to be 0.2006 at 25°. This value is consistent with the best extrapolations within a few tenths of a millivolt.

The temperature coefficient of E^0 was obtained by combining the temperature coefficient of the cadmium amalgam electrode[15b]

$$\mathrm{d}E^0_{\mathrm{Cd-Hg}}/\mathrm{d}t = 0.000289 - 0.00000194(t - 25) \qquad (9)$$

where t is in degrees C., with that of the silver–silver iodide electrode as given by Owen[16,20]

$$\mathrm{d}E^0_{\mathrm{AgI}}/\mathrm{d}t = 0.000328 + 0.0000072(t - 25) \qquad (10)$$

Combining $E^0_{25} = 0.2006$ with integrated forms of equations (9) and (10) and transforming to absolute temperature gives

$$E^0_T = 0.0026865T - 0.00000457T^2 - 0.19415 \qquad (11)$$

Activity Coefficients.—Stoichiometrical activity coefficients were calculated by equation (3) from the electromotive forces at round molalities. Results of the calculation at the eight temperatures are tabulated in Table III. Hamer, Burton and Acree[21] have recently listed $2k$ in absolute volts at a number of temperatures as calculated from the most reliable values of the faraday and the gas constant. These values of k were converted to international volts by dividing by the factor 1.00034.[22] The quantities E^0 and k used in computing the activity coefficients are given in Table IV.

The activity coefficients at 25° are in good agreement with the values calculated from measurements of the cadmium–mercurous iodide cell,[6b] as may be seen in Fig. 1 where differences between log γ previously reported and those values (log γ_{B}) obtained in the present investigation are plotted as a function of the square root of the molality. The measurements of Getman[6a] were

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[17] Gould and Vosburgh, THIS JOURNAL, 62, 1817 (1940).

[18] Vosburgh, *ibid.*, 50, 2886 (1928).

[19] Bates and Vosburgh, *ibid.*, 59, 1188 (1937).

[20] The temperature coefficient of this electrode between 10 and 40° found by Gould and Vosburgh (ref. 17) is $\mathrm{d}E^0_{\mathrm{AgI}}/\mathrm{d}t = 0.000328 + 0.0000056(t - 25)$. Use of this equation in place of that of Owen would result in differences of about 1% in γ_{40}, changes in $(\bar{L}_2)_{40}$ of about 300 cal. and a lowering of $(\bar{C}_p - \bar{C}^0_p)_{25}$ by 22 cal.

[21] Hamer, Burton and Acree, *J. Research Nat. Bur. Standards*, 24, 269 (1940).

[22] Wensel, *ibid.*, 22, 375 (1939).

TABLE III

STOICHIOMETRICAL ACTIVITY COEFFICIENTS OF CADMIUM IODIDE

m	γ_5	γ_{10}	γ_{15}	γ_{20}	γ_{25}	γ_{30}	γ_{35}	γ_{40}
0.002	0.566	0.583	0.596	0.607	0.615	0.622	0.626	0.629
.005	.445	.460	.472	.483	.492	.499	.503	.506
.007	.391	.405	.417	.428	.436	.443	.447	.440
.01	.338	.352	.364	.374	.382	.389	.394	.397
.02	.243	.254	.265	.274	.281	.287	.291	.294
.05	.141	.148	.156	.162	.167	.171	.174	.177
.07	.113	.120	.126	.131	.135	.139	.142	.143
.1	.0891	.0942	.0989	.103	.107	.110	.112	.113
.2	.0562	.0595	.0625	.0652	.0675	.0694	.0708	.0718
.5	.0307	.0325	.0342	.0356	.0369	.0379	.0387	.0393
.7	.0254	.0268	.0282	.0294	.0304	.0312	.0318	.0323
1.0	.0210	.0222	.0233	.0242	.0250	.0257	.0262	.0265
1.5	.0173	.0182	.0191	.0198	.0205	.0210	.0213	.0216
2.0	.0155	.0163	.0171	.0177	.0183	.0187	.0190	.0192

TABLE IV

STANDARD POTENTIALS. VALUES OF k

t	E^0	k
5	0.19955	0.02758
10	.20016	.02808
15	.20053	.02857
20	.20069	.02907
25	.20060	.02957
30	.20029	.03006
35	.19975	.03056
40	.19898	.03105

recalculated with the use of $E^0_{25} = 0.2511$.[23] For comparison, γ_{25} was also computed from freezing point measurements[6d] with the use of the heats of dilution reported in this paper. Activity coefficients that agree well with those of Table III have been obtained by Robinson and Wilson[6e] from isopiestic vapor pressure measurements between 0.1 m and saturation with the use of the 0.2 m electromotive force result of Bates and Vosburgh as a point of reference.

Relative Partial Molal Heat Content and Relative Partial Molal Specific Heat.—The partial molal heat content, $\overline{L}_2$, and partial molal specific heat, $\overline{C}_p - \overline{C}_p^0$, of cadmium iodide relative to the infinitely dilute solution of the salt were computed in the usual way from the first and second derivatives, respectively, of electromotive force with temperature. The equations employed in the calculation are

$$\overline{L}_2 = \alpha + \beta T^2 \qquad (12)$$

and

$$\overline{C}_p - \overline{C}_p^0 = 2\beta T \qquad (13)$$

where α is -46148 (A + 0.19415) and β is 46148 (C + 0.00000457). Values of the constants α and β are listed in Table V. The fourth and fifth columns of the table give L_2 and $\overline{C}_p - \overline{C}_p^0$

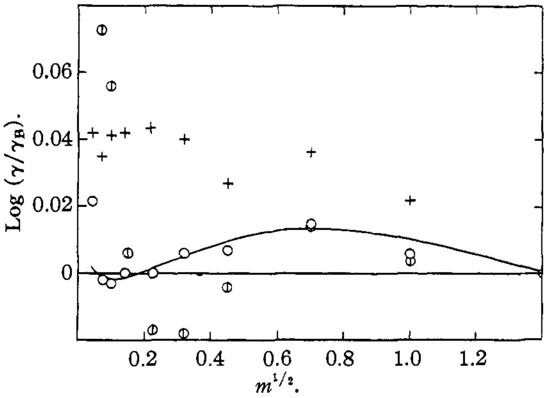

Fig. 1.—Log (γ/γ_B) at 25° as a function of square root of the molality. Crosses represent log (γ/γ_B) when γ is computed from freezing point measurements; open circles are values obtained with the mercury–mercurous iodide cell (ref. 6b), and marked circles are from the silver-silver iodide cell measurements of Getman (ref. 6a).

TABLE V

RELATIVE PARTIAL MOLAL HEAT CONTENT AND RELATIVE PARTIAL MOLAL SPECIFIC HEAT OF CADMIUM IODIDE

m	$-\alpha$	β	$(\overline{L}_2)_{298.2}$, cal.	$(\overline{C}_p - \overline{C}_p^0)_{298.2}$, cal.
0.002	11034	0.1094	−1308	65
.005	13848	.1371	−1660	82
.007	14849	.1463	−1840	87
.01	16325	.1601	−2086	96
.02	19218	.1878	−2516	112
.05	21762	.2109	−3008	126
.07	21884	.2109	−3130	126
.1	21948	.2109	−3194	126
.2	22011	.2109	−3257	126
.5	22019	.2109	−3265	126
.7	21945	.2109	−3191	126
1.0	21849	.2109	−3095	126
1.5	21692	.2109	−2938	126
2.0	21506	.2109	−2752	126

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[23] The standard potential of the cadmium (metal)–silver iodide cell of Getman was obtained by adding the potential of the cell, Cd(s) | Cd^{++} | Cd-Hg, found by Parks and La Mer, THIS JOURNAL, **56**, 90 (1934), to have a value of 0.0505 at 25°, to the E^0 of cell (1).

at 298.2° K. The relative partial molal heat content at 5, 25 and 40° is plotted in Fig. 2 as a function of the square root of the molality.

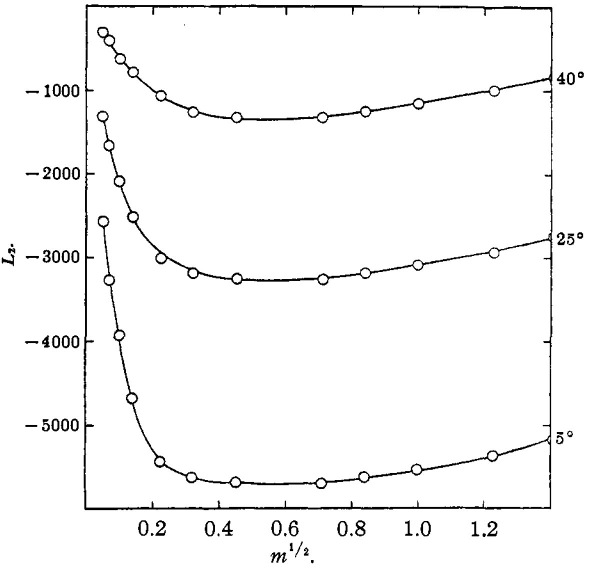

Fig. 2.—Relative partial molal heat content of cadmium iodide at 5, 25 and 40° as a function of the square root of the molality; diameter of circles, 120 cal.

Cadmium chloride, bromide and iodide form a regular series of decreasing activity in solution. It is of interest to compare these three abnormal electrolytes likewise with respect to their relative partial molal heat contents (heats of dilution) and relative partial molal specific heats. It may be clearly seen from Figs. 3 and 4 that the enhanced ionic association as we pass from the chloride to the iodide is attended by a decrease in $\bar{L}_2$ but an increase in its temperature coefficient, $d\bar{L}_2/dt = \bar{C}_p - \bar{C}_p^0$.

The author is pleased to acknowledge the kind assistance of Professor Herbert S. Harned.

Summary

1. Electromotive force measurements of the cell

Cd–Hg (2-phase) | CdI_2 (m) | AgI–Ag

have been made at intervals of 5° over the range of temperature, 5 to 40°. The molality of cadmium iodide was varied from 0.002 to 2. The standard potential of the cell was evaluated.

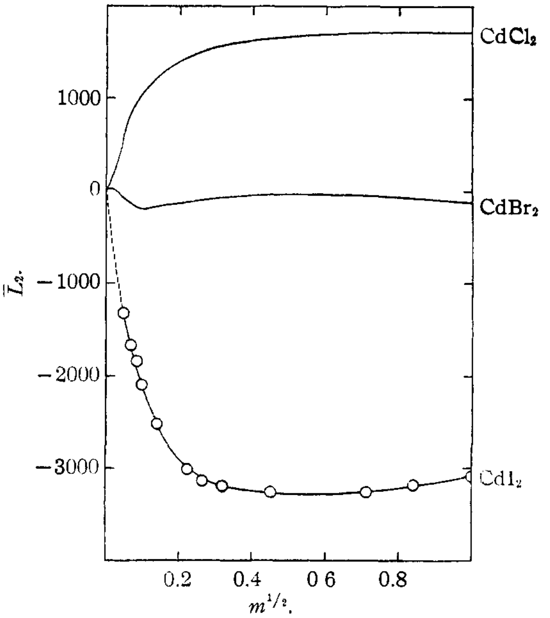

Fig. 3.—Comparison of relative partial molal heat contents of cadmium halide solutions at 25°.

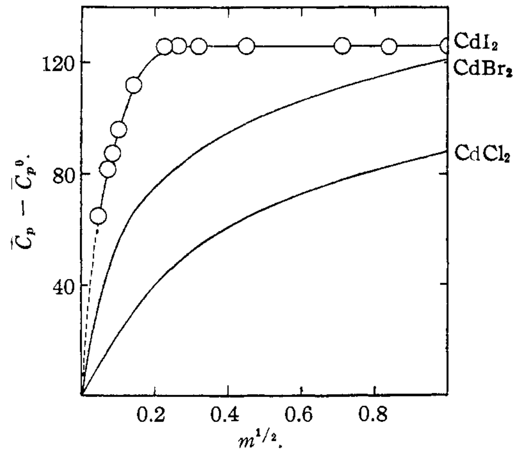

Fig. 4.—Comparison of relative partial molal specific heats of cadmium halide solutions at 25°.

2. The stoichiometrical activity coefficients, the relative partial molal heat content and the relative partial molal specific heat of cadmium iodide in aqueous solution have been calculated. Comparisons with cadmium chloride and cadmium bromide were made.

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