[CONTRIBUTION FROM THE STERLING CHEMISTRY LABORATORY OF YALE UNIVERSITY]

The Thermodynamics of Bi-univalent Electrolytes. III. Zinc Iodide in Aqueous Solution[1]

BY ROGER G. BATES[2]

The thermodynamic behavior of zinc iodide in aqueous solution is of interest in relation to the problem of the intermediate electrolyte. Cadmium iodide has been shown[1b,3,4] to represent an extreme case of incomplete dissociation in solution. Little is known, however, regarding the degree to which this abnormality extends to zinc iodide.

Van Name and Brown found[5] that the tri-iodide equilibrium constant determined with zinc iodide–iodine solutions retained its normal value over a considerable range of electrolyte concentration. Grimm has likewise reported[6] lattice energy calculations for zinc iodide that lead one to expect a high degree of electrolytic dissociation of the salt in solution. A forty-eight-hour exposure of a concentrated zinc iodide solution failed to yield any perceptible Raman lines,[7] although a strong iodine coloration may have interfered.

The transference studies of Hittorf, on the other hand, have shown[8] that the transference number of zinc becomes negative in strong solutions of zinc iodide, while Van Rysselberghe, Grinnell and Carlson found[9] that the conductivities of zinc iodide–potassium iodide mixtures showed large deviations from the mixture rule above a total concentration of 4 N.

Measurements of the electromotive force of the cell

$$\text{Zn–Hg (2-phase)/ZnI}_2\ (m)\text{/AgI–Ag} \qquad (1)$$

have been made at 5° intervals from 5 to 40°, inclusive, and over a range of zinc iodide molality extending from 0.005 to 0.8. From the results, the standard potential of the cell has been evaluated, and calculations of the activity coefficients, relative partial molal heat content and relative partial molal specific heat of the salt have been made. Zinc iodide in aqueous solution has been found to behave as a normal bi-univalent electrolyte over the range of concentration studied.

Experimental Methods

An amalgam containing 5% of zinc by weight was used in most of the cells, although preparations containing as little as 4.5% zinc or as much as 5.5% were tried without noticeable difference in results. According to Puschin,[10] these amalgams are saturated over the temperature range studied. The best grade of Kahlbaum zinc and thrice-distilled mercury were employed, and the preparations were stored under hydrogen in an amalgam pipet. Previous to the preparation of each electrode, the pipet was warmed in an oven until its contents were entirely fluid; a portion of amalgam was then drawn through an ungreased stopcock of large bore into the evacuated cell vessel. The electrodes used in this work were shown to be identical with a zinc amalgam electrode prepared from a sample of spectroscopically pure zinc kindly furnished by the Research Laboratory of the New Jersey Zinc Co.

The silver–silver iodide electrodes were formed on small platinum spirals by the thermal decomposition of a paste composed of 90% silver oxide and 10% silver iodide. Ten to fifteen minutes at about 450° was found to be a satisfactory decomposition time. Silver iodide was prepared by precipitation and was digested three days under water at about 80°. It was found necessary to employ electrodes of 20–25% silver iodide for measurements in zinc iodide solutions stronger than 0.2 molal. The solubility of silver iodide in iodide solutions rises extremely rapidly as the iodide ion concentration is taken above about 0.4 gram ions per liter.

Electrodes prepared by the decomposition of oxide–iodate mixtures by the method of Owen[11] were tried and found to be less reproducible in the more concentrated zinc iodide solutions than those prepared from oxide–iodide mixtures. It has been shown recently[12] that silver iodate decomposes at about 390° but that a period of one to two hours is required for complete decomposition at 400 or 450°. Table I gives a comparison of the decomposition temperatures of the silver salts commonly used for thermal electrodes. It is evident that the high temperatures requisite for the complete and rapid decomposition of the iodate may cause considerable loss of silver iodide, whereas the same temperature is quite satis-

TABLE I

DECOMPOSITION TEMPERATURES OF SILVER SALTS

	$AgXO_3$	AgX
X = Cl	270°	1550° (boils)
X = Br	*ca.* 330	700
X = I	*ca.* 390	552

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[1] Previous papers in this series are (a) Bates and Vosburgh, THIS JOURNAL, **59**, 1583 (1937); and (b) Bates and Vosburgh, *ibid.*, **60**, 137 (1938).

[2] Sterling Fellow.

[3] McBain, Van Rysselberghe and Squance, *J. Phys. Chem.*, **35**, 999 (1931).

[4] Riley and Gallafent, *J. Chem. Soc.*, 514 (1932).

[5] Van Name and Brown, *Am. J. Sci.*, **44**, 105 (1917).

[6] Grimm, *Z. physik. Chem.*, **102**, 113, 141 (1922).

[7] Venkateswaran, *Proc. Ind. Acad. Sci.*, **1**, 850 (1935).

[8] Hittorf, *Pogg. Ann.*, **106**, 513 (1859).

[9] Van Rysselberghe, Grinnell and Carlson, THIS JOURNAL, **59**, 336 (1937).

[10] Puschin, *Z. anorg. Chem.*, **36**, 201 (1903).

[11] Owen, THIS JOURNAL, **57**, 1526 (1935).

[12] G. R. Cooper, M. A. thesis, Duke University, 1938.

TABLE II

ELECTROMOTIVE FORCES OF THE CELL

Zn-Hg (2-phase)/ZnI_2 (m)/AgI-Ag

m	E_5	E_{10}	E_{15}	E_{20}	E_{25}	E_{30}	E_{35}	E_{40}
0.001182					0.8584			
.002026					.8379			
.004140					.81190			
.004692	0.80114	0.80304	0.80475	0.80628	.80753	0.80862	0.80967	0.81057
.005683	.79510	.79689	.79855	.79983	.80103	.80212	.80296	.80365
.008455	.78235	.78403	.78531	.78645	.78739	.78829	.78888	.78944
.009650	.77791	.77934	.78064	.78174	.78271	.78347	.78408	.78453
.01277	.76871	.76995	.77114	.77223	.77302	.77365	.77417	.77422
.01801	.75742	.75858	.75952	.76028	.76088	.76131	.76165	.76170
.02675	.74515	.74607	.74680	.74739	.74782	.74802	.74814	.74810
.04294	.73023	.73085	.73135	.73165	.73189	.73185	.73159	.73122
.05619	.72103	.72156	.72187	.72212	.72222	.72204	.72173	.72121
.06068	.71853	.71905	.71939	.71955	.71957	.71944	.71915	.71872
.07441	.71239	.71267	.71281	.71286	.71286	.71261	.71216	.71163
.1224	.69573	.69572	.69563	.69540	.69502	.69439	.69360	.69270
.1771	.68283	.68268	.68241	.68198	.68138	.68070	.67985	.67889
.3289	.66015	.65960	.65896	.65820	.65725	.65618	.65504	.65375
.4176	.64983	.64911	.64827	.64735	.64629	.64515	.64386	.64251
.8008	.61789	.61671	.61551	.61425	.61292	.61158	.61011	.60864

factory for the formation of silver bromide and silver chloride.

Several zinc iodide stock solutions were used. These solutions were prepared by dissolving the salt, recrystallized from oxygen-free conductivity water, in a quantity of boiled conductivity water through which purified hydrogen had been bubbled for some time. The careful exclusion of air at all times was imperative. Zinc iodide reacts with oxygen and with carbon dioxide and is oxidized rapidly when in contact with cellulose, both in solution and in the solid condition.[13] Sintered glass filters were used in all filtrations.

Weighed samples of the stock solutions were analyzed for iodide by the Volhard method. All solutions were kept under hydrogen in flasks from which they could be expelled by hydrogen pressure as desired. Weighed amounts of water were added to weighed quantities of stock solution in making the dilutions. Vacuum corrections were made for all weighings. No precipitation of hydroxide or basic salt was observed.

The cells vessels were similar to those described by Bates and Vosburgh.[1a] To permit the use of the vessels in water thermostats, the electrode contacts were made through mercury wells. The use of Pyrex glass with tungsten contacts served to prevent the occasional breakage of vessels observed when zinc amalgam is in contact with sealed-in platinum wires.[14]

The process of making a cell was carried out entirely in the absence of air. The vessel, containing a silver iodide electrode and a portion of amalgam, was evacuated with an oil pump for ten to fifteen minutes and filled with hydrogen. Two portions of cell solution were admitted from a saturator flask to each arm of the vessel and expelled through the side tubes provided for the purpose. The cell electrolyte was then introduced.

Cells were made in triplicate at each concentration. Within the optimum range of concentration (0.01 to 0.2 m) triplicate cells deviated from the mean electromotive force by less than 0.1 mv. when equilibrium conditions had been attained, usually within two to five hours. Between 0.2 and 0.8 m, where the solubility of silver iodide in the electrolyte is large, the agreement was as satisfactory, but the time of attainment of equilibrium and the life of the cell were much shorter than was the case at the lower concentrations. Below 0.01 m the cells ordinarily required overnight to come to satisfactory equilibrium. The reproducibility was of the order of 0.2 mv. Temperature coefficient runs were completed within a period of ten hours after they were begun. It was observed that most of the cells began to decrease slowly in electromotive force after approximately thirty-six hours. A separate temperature run was made for each group of three cells. Upon change of temperature most of the cells attained constant values in twenty to thirty minutes, although marked hysteresis was noted in those with electrolytes more dilute than 0.005 molal. The temperature of initial measurement was 25°, and all cells were brought back to this temperature at the completion of the run. The original 25° values were usually satisfactorily resumed, and the results for cells showing unusual drifts during the run were rejected as unreliable.

The electromotive forces were measured by means of a Leeds and Northrup Type K potentiometer. The standard cell was frequently checked against the laboratory standards. Thermometers were standardized against a calibrated platinum resistance thermometer. The temperatures were probably accurate to ±0.03°.

Experimental Results

The electromotive forces obtained in the best runs are recorded in Table II. These values were fitted to the quadratic equation

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

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[13] Berridge, *B. A. Rep.*, 658 (1895).

[14] Cowperthwaite and La Mer, THIS JOURNAL, 53, 4333 (1931).

by the method of Harned and Nims.[15,16] The electromotive forces at 25° at round molalities were read from a large scale plot of E *versus* log m. These values are recorded in Table III with the smoothed a and b constants.

TABLE III

CONSTANTS OF EQUATION (2)

m	E_{25}	$a \times 10^6$	$b \times 10^6$
0.002	0.83845		
.003	.82360		
.005	.80556	241	−3.68
.007	.79392	206	−3.64
.008	.78930	193	−3.62
.01	.78150	169	−3.55
.02	.75780	96	−3.39
.03	.74395	55	−3.28
.05	.72654	3	−3.13
.07	.71502	− 31	−3.02
.1	.70256	− 67	−2.91
.2	.67683	−139	−2.64
.5	.63765	−233	−1.89
.7	.62018	−256	−1.31
.8	.61295	−263	−1.09
	E^0_{25}	$a_0 \times 10^6$	$b_0 \times 10^6$
E^0:	0.61055	−428	−3.91

The Standard Potential of the Cell

The electromotive force of cell (1) may be represented by the equation

$$E = E^0 - 2.3026(RT/2F) \log \mathbf{a}_{\mathrm{ZnI_2}} = E^0 - k \log 4m^3 \gamma_{\pm}^3 \quad (3)$$

in which E^0 is the standard potential of the cell, E the observed electromotive force, $\mathbf{a}_{\mathrm{ZnI_2}}$ the activity of zinc iodide in a solution of molality m, k equals $2.3026(RT/2F)$ and $\gamma_{\pm}$ is the stoichiometrical activity coefficient of zinc iodide.

The evaluation of E^0 may be accomplished, as pointed out by Hitchcock,[17] by the substitution of the Debye–Hückel limiting law

$$-\log \gamma_{\pm} = u'\sqrt{c} + Pc = u'\sqrt{md} + Pmd \quad (4)$$

in the right-hand term of equation (3) and extrapolating this function of the original electromotive forces to zero concentration, bearing in mind that in dilute solutions c, the molar concentration, is very nearly equal to md, where d is the density of the solution. The expression for $E^{0\prime}$, the apparent standard potential, then becomes

$$E^{0\prime} = E^0 + 3kPmd = E + k \log 4 + 3k \log m - 3k\, u'\sqrt{md} \quad (5)$$

in which u' is the limiting slope of the Debye–Hückel theory, varying inversely as $(DT)^{3/2}$, where D is the dielectric constant of the solvent[18] and T is the absolute temperature. P is an empirical constant. Equation (4) is valid only at extremely low concentrations of zinc iodide.

Scatchard and Tefft have shown[19] that the incomplete dissociation of the intermediate ion, MX^+, of a bi-univalent salt causes a hump in the plot of $E^{0\prime} - E^0$ against $c^{1/2}$. By the matching of theoretical plots constructed for various values of K_2, the dissociation constant of the intermediate ion, with the plot of experimental data it is possible to obtain an estimate of the second dissociation constant of the salt.[20] The character of the zinc iodide results when treated in this manner indicated a high degree of dissociation, with a constant greater than 10 for the ZnI^+ ionization process. Therefore, in the further treatment of the results complete ionization was assumed.

The activity coefficient in equation (3) may be represented with somewhat more accuracy by the Hückel equation[21]

$$-\log \gamma_{\pm} = \frac{u\sqrt{3c}}{1 + A\sqrt{3c}} + Bc - \log(1 + 0.054m) \quad (6')$$

or, less exactly

$$-\log \gamma_{\pm} = \frac{u\sqrt{\mu d}}{1 + A\sqrt{\mu d}} + B''\mu d \quad (6)$$

where μ is the ionic strength, $\mu = \sum m_i z_i^2/2 = 3m$, u is a constant related to u' of equation (4) by the expression, $u' = u\sqrt{3}$, B and B'' are empirical constants and

$$A = Ka \quad (7)$$

K is a quantity varying as $(DT)^{-1/2}$ and a is the mean distance of approach of the ions. This ion size parameter for a highly dissociated electrolyte is independent of temperature over the ordinary range of measurement.[14,22]

Since $3k \log (1 + 0.054m)$ amounts only to 0.09 mv. for $m = 0.05$, the highest concentration employed in obtaining E^0, the omission of the third term on the right of equation (6′) is of no appreciable influence on the course of the extrapolation. Combining equation (3) with equation (6) gives

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(15) Harned and Nims, THIS JOURNAL, **54**, 423 (1932).

(16) The average deviations of the observed electromotive forces at the eight temperatures from the quadratic equation were of the order of 0.02–0.05 mv. In no case was the average deviation greater than 0.1 mv.

(17) Hitchcock, *ibid.*, **50**, 2076 (1928).

(18) The equation of Wyman, *Phys. Rev.*, **35**, 623 (1930), was used in obtaining D at the eight temperatures.

(19) Scatchard and Tefft, THIS JOURNAL, **52**, 2272 (1930).

(20) Harned and Fitzgerald, *ibid.*, **58**, 2624 (1936).

(21) Hückel, *Physik. Z.*, **26**, 93 (1925).

(22) Harned and Ehlers, THIS JOURNAL, **55**, 2179 (1933).

$$E^{0\prime} = E^0 + B'\mu d = E + k\log 4 + 3k\log m - \frac{3ku\sqrt{\mu d}}{1 + A\sqrt{\mu d}} \qquad (8)$$

where $B' = 3kB''$.

Values of $E^{0\prime}$ were calculated by equation (8) and were extrapolated to zero ionic strength to obtain E^0. Figure 1 shows the extrapolations at the eight temperatures. The values of the various parameters of Hückel's equation are listed in Table IV, together with the a values that best fitted the experimental results. Approximate densities of the zinc iodide solutions were obtained from "International Critical Tables."[23]

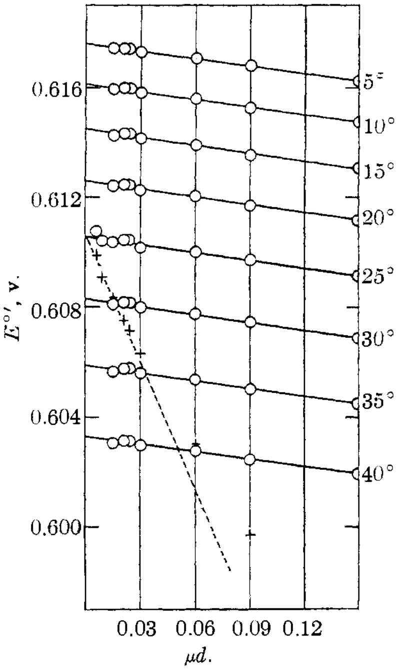

Fig. 1.—Extrapolation functions for cell (1). Circles represent plots of $E^{0\prime}$ according to equation (8). Crosses represent $E^{0\prime}$ according to equation (5). Diameter of circles, 0.4 mv.

TABLE IV

PARAMETERS OF EQUATIONS (6) AND (7)

t	u	$-B''$	$K \times 10^{-8}$	$a \times 10^8$ (cm.)
5°	0.9785	0.113	0.325	6.09
10	.9866	.111	.326	6.07
15	.9944	.109	.327	6.05
20	1.003	.107	.328	6.04
25	1.012	.105	.329	6.02
30	1.022	.103	.330	6.00
35	1.032	.102	.331	5.98
40	1.043	.100	.332	5.96

The crosses of Fig. 1 indicate $E^{0\prime}$ points at 25° calculated by equation (5), and the broken line has been drawn to intersect the equation (8) plot at $\mu = 0$. It is evident that the extrapolation with the use of the Debye–Hückel limiting law is rather uncertain. The E^0 obtained by the use of the extended equation, however, is thought to be quite reliable.

The standard potentials of cell (1) may be expressed by the equation

$$E^0_t = E^0_{25} + a_0(t - 25) + b_0(t - 25)^2 \qquad (9)$$

with an average deviation of 0.03 mv. The numerical values of the constants of this equation appear at the bottom of Table III.

Standard Potentials of Zinc Electrodes

In the second and third columns of Table V are listed the standard potentials, E^0, of the zinc–silver iodide cell at 5° intervals from 5 to 40° The potentials of the electrode, Zn-Hg (2-phase)/Zn^{++}(a = 1), are represented by $E^{0''}$ and are given in the fourth and fifth columns. These values were computed by subtracting the standard potentials of the hydrogen–silver iodide cell[11] from the standard potentials of cell (1) at corresponding temperatures. For the former cell, Owen has given the equation

TABLE V

STANDARD POTENTIALS

Zn-Hg/ZnI_2(a = 1)/AgI-Ag, E^0

Zn-Hg/Zn^{++}(a = 1), H^+(a = 1)/H_2, $E^{0''}$

t, °C.	E^0	E^0 (Eq. 9)	$E^{0''}$	$E^{0''}$ (Eq. 11)
5	0.6176	0.61755	0.76472	0.76462
10	.6161	.61609	.76415	.76417
15	.6145	.61444	.76370	.76371
20	.6126	.61259	.76322	.76323
25	.6105	.61055	.76275	.76274
30	.6083	.60831	.76226	.76223
35	.6059	.60588	.76176	.76171
40	.6033	.60325	.76117	.76117

$$E^0_{\rm HI} = -0.15219 - 328 \times 10^{-6}(t - 25) - 3.6 \times 10^{-6}(t - 25)^2 \qquad (10)$$

Subtraction of this equation from equation (9) gives

$$E^{0''} = E^0_{\rm Zn\text{-}Hg/Zn^{++}} = 0.76274 - 0.0001(t - 25) - 0.00000031(t - 25)^2 \qquad (11)$$

Since Clayton and Vosburgh[24] have shown that the electromotive force of the cell, Zn(s)/Zn^{++}/Zn-Hg (5%), is zero, it is evident that $E^{0''}$ likewise represents the standard potentials of the zinc metal electrode.

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[23] "International Critical Tables," McGraw-Hill Book Co., Inc., New York, N. Y., 1928, Vol. III, p. 65.

[24] Clayton and Vosburgh, THIS JOURNAL, 58, 2093 (1936).

Recorded standard potentials for the zinc amalgam electrode do not agree well. Shrawder, Cowperthwaite and La Mer[25] computed the potential of this electrode from the standard potential of the zinc amalgam–lead sulfate cell[14] and an E^0 for the lead amalgam–lead sulfate electrode[26] finding a value of 0.7614 v. at 25°.

From measurements of the cell

$$\text{Zn-Hg (2-phase)}/\text{ZnCl}_2\ (m)/\text{AgCl-Ag} \qquad (12)$$

at 25° and accepted data on the Ag–AgCl electrode, Scatchard and Tefft[19] found a zinc amalgam electrode potential of 0.7610 v., while Brüll[27] calculated a value of 0.7596 v. from electromotive forces of zinc amalgam–mercurous chloride cells with zinc chloride electrolytes. The low result of Brüll can be attributed largely to the use of too high a calomel electrode potential (0.2700 v.) for the computation. Gerke[28] and Randall and Young[29] agree that the mercury–mercurous chloride electrode is 0.0455 v. more positive than the silver–silver chloride electrode, which has a value of 0.2224 v. at this temperature.[22] Subtraction of 0.2679 v. from the standard potential of Brüll's cell gives 0.7617 v. for the potential of the zinc amalgam electrode.

The E^0 of Scatchard and Tefft, and of Brüll as well, was obtained by the Hitchcock method, using an extrapolation function similar to equation (5). Since the Hückel equation gives a much more valid representation of the activity coefficient of zinc chloride than does the limiting law in solutions more concentrated than 0.005 M, it seemed worthwhile to extrapolate the results with the use of equation (8). The circles of Fig. 2 represent $E^{0\prime}$ values of Scatchard and Tefft, while the crosses indicate values of the quantity $E^{0\prime} - 0.0455$ calculated from Brüll's electromotive forces. The broken line again shows the course of the Hitchcock extrapolation. An apparent ionic diameter of 5.4 Å. made equation (8) fit the results to best advantage. Triangles represent $E^{0\prime}$ values when the parameter a is 4.0 Å., and dots were calculated for a = 6.1 Å. Inspection of $E^{0\prime}$ points computed with the three different a parameters shows that the μ = 0.13 point lies about 1 mv. too high. With this exception, the results of Scatchard and Tefft between 0.007 and 0.1 m give an unambiguous straight line extrapolation to an E^0 of 0.9850 v.; the three results of Brüll in the same range of concentration lie about 0.5 mv. higher. Below 0.007 m the $E^{0\prime}$ values of both investigations show a decrease. Scatchard and Tefft observed[19] the decreasing electromotive force of cell (12) when air was allowed to come in contact with the amalgam. Although imperfect exclusion of oxygen from the dilute solutions would explain the drop in $E^{0\prime}$, it is possible that failure of the cells to attain equilibrium conditions during the period of measurement was responsible.

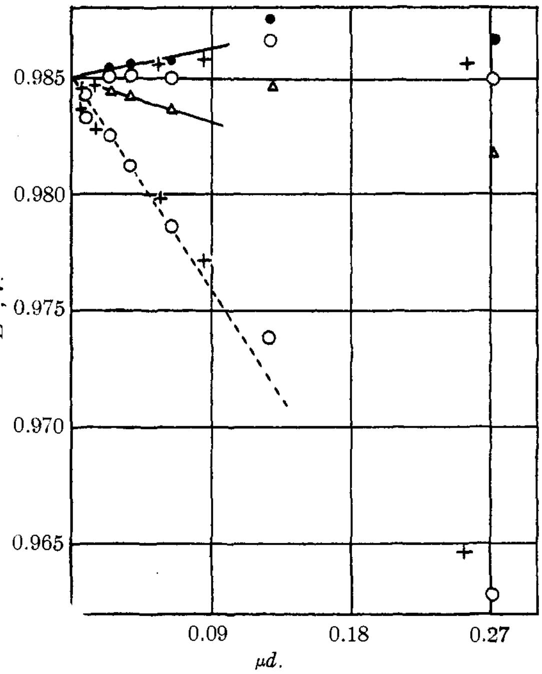

Fig. 2.—Extrapolation of electromotive forces of cell (12) to zero ionic strength at 25°. Crosses represent $E^{0\prime} - 0.0455$ computed from measurements of Brüll.[27] Dots, circles and triangles represent $E^{0\prime}$ from data of Scatchard and Tefft.[19] Lower points were calculated by equation (5), upper points by equation (8) using a = 6.1 Å. (dots), 5.4 Å. (circles) and 4.0 Å. (triangles). Diameter of circles, 0.5 mv.

It seems likely that Scatchard and Tefft, in extrapolating to 0.9834 v., placed undue weight upon a low 0.003 m (μ = 0.009) point. On the other hand, the extrapolation to 0.9850 v. by equation (8) places considerable weight on the three next higher concentrations, μ = 0.023, 0.037 and 0.064. These points, however, represent electromotive force measurements within the optimum concentration range of zinc chloride.

Figure 2 makes it seem probable that the standard potential of cell (12) at 25° lies between

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[25] Shrawder, Cowperthwaite and La Mer, THIS JOURNAL, **56**, 2348 (1934).

[26] Shrawder and Cowperthwaite, *ibid.*, **56**, 2340 (1934).

[27] Brüll, *Gazz. chim. ital.*, **64**, 261 (1934).

[28] Gerke, THIS JOURNAL, **44**, 1684 (1922).

[29] Randall and Young, *ibid.*, **50**, 989 (1928).

TABLE VI

ACTIVITY COEFFICIENTS OF ZINC IODIDE

m	γ_5	γ_{10}	γ_{15}	γ_{20}	γ_{25}	γ_{30}	γ_{35}	γ_{40}
0.002					0.851			
.003					.833			
.005	0.808	0.803	0.802	0.800	.799	0.797	0.796	0.793
.007	.782	.776	.775	.774	.772	.770	.768	.765
.008	.772	.767	.765	.763	.761	.759	.757	.754
.01	.757	.751	.750	.748	.746	.744	.741	.738
.02	.701	.696	.694	.692	.690	.687	.684	.680
.03	.671	.666	.664	.661	.659	.655	.652	.648
.05	.634	.628	.627	.624	.621	.617	.613	.609
.07	.611	.606	.604	.601	.598	.594	.590	.585
.1	.592	.587	.585	.582	.578	.574	.570	.564
.2	.581	.575	.572	.569	.564	.559	.553	.546
.5	.650	.643	.638	.631	.624	.614	.604	.593
.7	.740	.730	.723	.713	.701	.687	.672	.656
.8	.787	.775	.766	.754	.740	.724	.706	.687

0.9845 and 0.9852 v. and, consequently, that the zinc amalgam electrode potential has a value lying between 0.7621 and 0.7628 v. This conclusion is in satisfactory accord with the value of 0.7627 v. obtained in this investigation.

Activity Coefficients

The stoichiometrical activity coefficients of zinc iodide have been calculated by equation (3) and are given in Table VI.

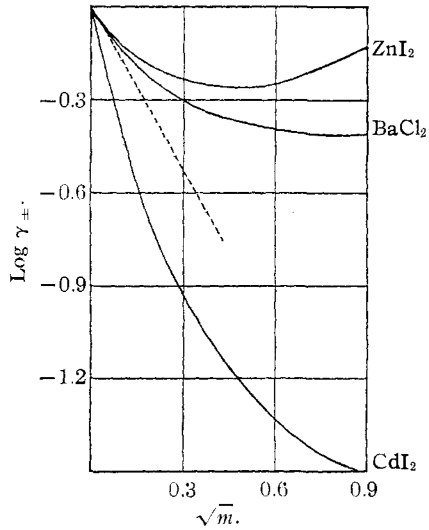

Fig. 3.—Logarithm of the stoichiometrical activity coefficients of zinc iodide, barium chloride and cadmium iodide as a function of the square root of the molality. The Debye–Hückel limiting slope is indicated by the broken line.

From an inspection of the slopes of the extrapolation plots of Fig. 1 it is clear that B' of equation (8) changes little with the temperature and has a value of -0.0093. The corresponding B'' values of equation (6) have been evaluated by dividing this quantity by $3k$ at each temperature and are given in the third column of Table IV. Equation (6), with the use of the parameters given in Table IV and a d value of unity, represents the activity coefficient of zinc iodide over the entire range of molality studied with an accuracy better than 1%.

In Fig. 3 is plotted log $\gamma_\pm$ at 25° against $m^{1/2}$. Plots of the barium chloride activity coefficients as determined by Tippetts and Newton[30] and of the cadmium iodide results of Bates and Vosburgh[1a] have been included for comparison. The broken line indicates the Debye–Hückel limiting slope. The activity of zinc iodide in solution is somewhat greater than that of barium chloride at the same molality and is considerably greater than that of the slightly dissociated cadmium iodide.

Relative Partial Molal Heat Content

The partial molal heat content (heat of transfer) relative to an infinitely dilute solution of zinc iodide was computed from the temperature coefficients of electromotive force by the use of the Gibbs–Helmholtz equation

$$\bar{L}_2 = \bar{H}_2 - \bar{H}_2^0 = \Delta H - \Delta H^0 = -nF\left[E - E^0 - T\left(\frac{dE}{dT}\right) + T\left(\frac{dE^0}{dT}\right)\right] \quad (14)$$

With the substitution of $t = T - 273.1$, the quadratic equations (2) and (9) were made to express the variation of electromotive force (or standard potential) as a function of absolute temperature:

$$E_T = A + BT + CT^2 \quad (15)$$
$$E^0_T = A_0 + B_0T + C_0T^2 \quad (16)$$

These relationships are valid only between T =

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(30) Tippetts and Newton, THIS JOURNAL, **56**, 1675 (1934).

278.1 and 313.1°K. Equations (15) and (16) were substituted in equation (14), and the indicated differentiation was performed. Since $n = 2$ for zinc iodide, the expression becomes

$$\overline{L}_2 = -2F(A - A_0) + 2F(C - C_0)T^2 = \alpha + \beta T^2 \qquad (17)$$

Equation (17) is the equation of Harned and Thomas.[31] Values of α and β for zinc iodide solutions from 0.005 to 0.8 m are given in Table VII.

TABLE VII

CONSTANTS OF EQUATIONS (17) AND (19). $\overline{L}_2$ AND $\overline{C}_p - \overline{C}_p^0$

m	$-\alpha$	$\beta \times 10^4$	$(\overline{L}_2)_{298}$	$(\overline{C}_p - \overline{C}_p^0)_{298}$
			(calories)	
0.005	739	106	204	6
.007	848	125	259	7
.008	895	134	294	8
.01	1152	166	324	10
.02	1719	240	413	15
.03	2095	291	488	18
.05	2623	360	576	22
.07	3009	411	640	25
.1	3381	461	720	28
.2	4291	586	917	35
.5	6852	932	1432	56
.7	8740	1200	1922	72
.8	9405	1301	2160	78

Figure 4 is a plot of $\overline{L}_2$ against $m^{1/2}$ at 5, 15, 25 and 40°. The broken line shows the Debye–Hückel limiting slope for $\overline{L}_2$ at 25°

$$\overline{L}_2 = 3041\,c^{1/2} \qquad (18)$$

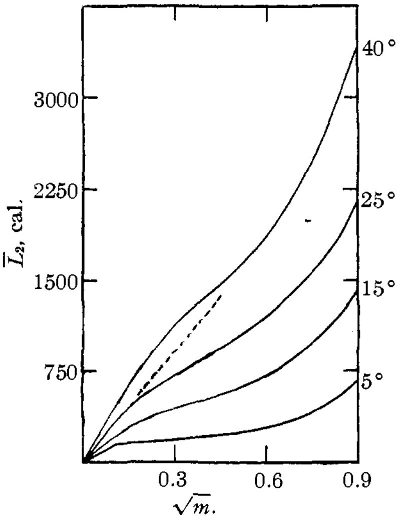

Fig. 4.—The relative partial molal heat content, $\overline{L}_2$, as a function of the square root of the molality. The broken line represents the limiting slope at 25°.

Unfortunately, no extensive calorimetric determinations of the heat contents of zinc iodide solutions have been made, and no estimate of the accuracy of the other quantities derived from the electromotive force data can be obtained from that source.

Relative Partial Molal Specific Heat

The values of the relative partial molal specific heat of zinc iodide were calculated by the equation

$$\overline{C}_p - \overline{C}_p^0 = \left(\frac{\partial \overline{L}_2}{\partial T}\right)_p = 2\beta T \qquad (19)$$

The change of $\overline{C}_p - \overline{C}_p^0$ with temperature is small in the dilute solutions and amounts to but 0.5 calorie per degree at 0.8 m. The $\overline{L}_2$ and $\overline{C}_p - \overline{C}_p^0$ values for zinc iodide solutions at 25° are given in Table VII. The latter values, computed from second derivatives of the experimental results, must be considered as only approximate.

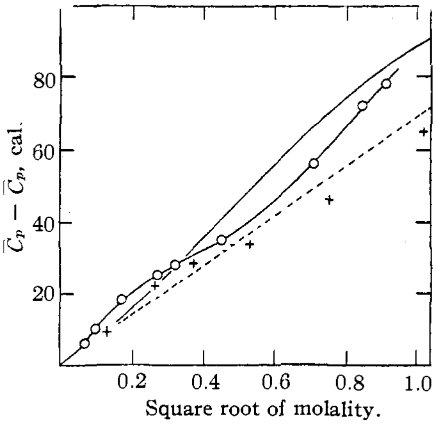

Fig. 5.—Relative partial molal specific heat at 25° as a function of the square root of the molality. Circles represent zinc iodide; crosses are for barium chloride, unbroken line for sodium sulfate. The broken line shows the limiting slope.

In Fig. 5, $\overline{C}_p - \overline{C}_p^0$ for zinc iodide is compared with the relative partial molal specific heat of sodium sulfate, computed by Randall and Rossini[32] from calorimetric data. The crosses represent values of the same quantity for barium chloride calculated by the author from the specific heats given by Richards and Dole.[33] The limiting slope of the Debye–Hückel theory is indicated by the broken line.

Grateful acknowledgment is made of the kind assistance of Professor Herbert S. Harned.

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

[32] Randall and Rossini, *ibid.*, **51**, 323 (1929).

[33] Richards and Dole, *ibid.*, **51**, 794 (1929).

Summary

1. Electromotive force measurements of the cell

Zn–Hg (2-phase)/ZnI_2 (m)/AgI–Ag

have been made at 5° intervals from 5 to 40° and at molalities of zinc iodide from 0.005 to 0.8.

2. The standard potential of the cell has been evaluated, and from it the electromotive forces of the hypothetical cells

Zn (s)/Zn^{++} (a = 1), H^+ (a = 1)/H_2, and
Zn–Hg (2-phase)/Zn^{++}(a = 1), H^+ (a = 1)/H_2

have been computed from 5 to 40°.

3. Calculations of the stoichiometrical activity coefficient, relative partial molal heat content and relative partial molal specific heat of zinc iodide in aqueous solution have been made.

4. Zinc iodide has been shown to be a normal bi-univalent electrolyte in aqueous solutions more dilute than 0.8 molal. Whereas the abnormalities of incomplete dissociation and complex ion formation indicated by transference and conductivity studies of strong zinc iodide solutions cause profound changes in the behavior of the salt in the concentrated range, they are of inappreciable influence below 0.8 m.

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[CONTRIBUTION FROM THE CHEMICAL LABORATORIES OF WASHINGTON SQUARE COLLEGE, NEW YORK UNIVERSITY]

A Rapid Method for Traces of Metals by the Dropping Mercury Electrode[1]

BY RALPH H. MÜLLER AND JOHN F. PETRAS

Introduction

In developing and testing the cathode ray tube polarograph[2] the authors required some means for obtaining the conventional Heyrovsky current–potential curves. It is obvious that these can be obtained manually and indeed the earliest studies were made in this fashion. It was to relieve the tedium of this procedure that Heyrovsky developed the automatically recording polarograph. The polarograph has the further advantage of providing a permanent record. On the other hand, the "manual" curves may be obtained with relatively inexpensive and commonly available equipment. The marked symmetry of the curves at once suggests a simple and rapid increment method for determining the concentration of a given ion.[2a] The object of this paper is to demonstrate the validity of the increment method and to illustrate its applicability.

Apparatus

It is common knowledge that a potentiometer will deliver at its e. m. f. terminals the potential which is set on the dials. In our work a Leeds and Northrup student-type potentiometer was used to deliver the desired potentials. The working current of the potentiometer was balanced against a standard cell in the usual manner. The e. m. f. terminals were connected to the electrode vessel in series with a wall-type galvanometer L and N Type P, 103 megohm sensitivity, resistance 126 ohms, period 8.9 sec. The latter was used in conjunction with an Ayrton shunt carefully adjusted to provide the critical damping resistance. The suspension was turned so that readings could be taken over more than half the scale length. The entire assembly was calibrated for linearity of response and used over that range. The electrode was of the type commonly used in polarographic work,[3] and consisted of a small Erlenmeyer flask with a platinum wire inseal for making connection with the mercury anode, and a bubbler inseal for flushing the contents of the vessel with hydrogen. The capillaries for the dropping mercury cathode were hand drawn from 1-mm. capillary tubing. They were graded for suitable lumen by examination under a low power microscope fitted with a micrometer ocular. The vessel was also provided with a salt bridge communicating with a saturated calomel electrode. In this way the anode potential could be measured. A switching arrangement enabled the operator to check the anode potential with the potentiometer. The mercury dropping rate was controlled by the pressure unit previously described.[2] It was found to be far more convenient and flexible.

Solutions

The solutions used in this work were prepared from reagent quality chemicals without further purification. Eastman purified de-ashed gelatin was added to all solutions to give a final concentration of 0.2%. A wide choice of addition agents is feasible. In routine work,

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[1] Presented before the Microchemical Division of the American Chemical Society, Milwaukee, Wisconsin, Meeting, September, 1938.

[2] R. H. Müller, R. L. Garman, M. E. Droz and J. F. Petras, *Ind. Eng. Chem., Anal. Ed.*, **10**, 339 (1938).

[2a] After this paper was submitted for publication the authors learned of similar work by Petering and Daniels in which the increment technique has been applied to the micro-analysis of oxygen. Their application undoubtedly precedes this contribution, and we regard our work as a general confirmation of the validity of the increment principle. The senior author is indebted to Professor Daniels for helpful discussion and exchange of opinions at the Milwaukee meeting and subsequently at his laboratory in Madison.

[3] J. Heyrovsky, in W. Böttger, "Physikalische Methoden der chemischen Analyse," Akademische Verlagsgesellschaft m. b. H., Leipzig, 1935; Hohn, "Chemische Analysen mit dem Polarographen," Verlag von Julius Springer, Berlin, 1937.