

## THE ACTIVITY COEFFICIENTS AND TRANSPORT NUMBERS OF ZINC BROMIDE AT 25° C. FROM E.M.F. MEASUREMENTS.

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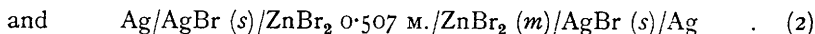
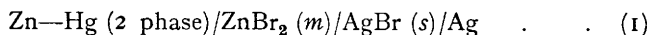
The thermodynamic study of a highly soluble ternary electrolyte such as zinc bromide has several points of interest. Fused salts and dilute solutions have been extensively studied but little work has been done in very strong solutions which may approach the conditions of the molten salt. Ternary electrolytes provide the problem of the intermediate ion. In the more dilute solutions evidence for or against complete dissociation of such electrolytes is desirable. Properties of strong solutions have frequently been interpreted in terms of complex ions. Measurements of transport numbers, mainly by Hittorf's method, have been interpreted on this basis. In the case of the zinc halides, Hittorf<sup>1</sup> found the anion transport number of zinc chloride to be 1.241 at 4.035 M., and the cation transport number is hence negative. Foxton and Shutt<sup>2</sup> studied the same salt at 60° C. and 80° C., by E.M.F. measurements on cells with and without liquid junction, and attributed the difficulty of interpreting their results to extensive formation of a complex anion.

Measurements are reported here at 25° C. of cells with and without liquid junction containing aqueous solutions of zinc bromide up to saturation. From them have been calculated a value for the standard

<sup>1</sup> Hittorf, *Z. physik. Chem.*, 1903, **43**, 249.

<sup>2</sup> Foxton and Shutt, *Trans. Faraday Soc.*, 1927, **23**, 480.

potential of the zinc electrode, and the activity coefficients and transport numbers of zinc bromide in the solutions. The cells were



### Experimental.

A strong solution of Hopkins and Williams  $\text{ZnBr}_2$  was made, and was light brown due to organic impurities. It was made slightly acid with  $\text{HBr}$ , boiled with pure finely-divided  $\text{Zn}$  to remove traces of heavy metals, and filtered through asbestos; then boiled with  $\text{Br}_2$  to oxidise organic matter, excess  $\text{Br}_2$  being removed by boiling with  $\text{Zn}$ . The solution was finally filtered by a Jena sintered glass filter, and the now colourless solution crystallised. After centrifuging the crystals, a saturated solution about 17 m. was made up and analysed for  $\text{Zn}$  and  $\text{Br}$ . The latter was in slight excess, and the calculated amount of  $\text{ZnO}$  was added to rectify this. The remaining solutions were made by weight dilution from this stock, and analysed for  $\text{Zn}$  only.  $\text{Zn}$  estimations were made by potassium ferrocyanide titration with diphenylbenzidine as indicator and  $\text{Br}$  estimations gravimetrically, and also by  $\text{AgNO}_3$  titration with eosin as absorption indicator.

A second stock solution was used for the solutions between 1.228 m. and 0.02 m. This was made by allowing pure  $\text{Zn}$  to react with pure  $\text{Br}_2$  beneath constant boiling  $\text{HBr}$ , the resulting solution being crystallised and the crystals treated as above to make a 3 m. stock solution.

The silver-silver bromide electrodes were analogous to Carmody's<sup>3</sup>  $\text{AgCl}$  electrodes,  $\text{Ag}$  being precipitated electrolytically on  $\text{Pt}$  gauze squares from a solution of potassium silver cyanide carefully freed from excess cyanide. Prolonged washing, three days in distilled water frequently changed, was required to give electrodes reproducible to 0.05 mv. These were greenish yellow in colour. The  $\text{Zn}$  electrodes were amalgamated  $\text{Zn}$  rods.

Above 1 m., oxygen had no effect on the  $\text{Zn}$  electrode, and measurements of the cell without liquid junction were made in an H-vessel with a large tap in the connecting tube. Above 5 m. this had to be kept closed, since  $\text{AgBr}$  was slowly dissolved from the electrode, and if permitted to diffuse to the  $\text{Zn}$  electrode, caused a drift in the E.M.F. Below 1 m. measurements were made under nitrogen, the gas being passed through the solution for three hours in a suitable cell. The cell with liquid junction was of the type used by Lucasse,<sup>4</sup> modified to lessen the chance of the solutions mixing, and gave excellently reproducible results, constant for over twelve hours. In all cells, one of the solutions was 0.507 m.

Forty solutions were measured between 0.02 m. and 16 m., spaced evenly so that satisfactory curves were obtained for interpolation to round concentrations.

### Experimental Results.

In Table I the complete data are given at round molalities, obtained from a large scale plot of the experimental voltages for the two types of cell against  $\log m$ . The first column gives the molality  $M$ , the second  $E$ , the E.M.F. of the corresponding cell without liquid junction, and the third the corresponding activity coefficient calculated as described below. The fourth column gives  $E_t$ , the E.M.F. of the cell with transport, one solution of concentration  $m$ . and the other 0.507 molal. In the fifth

<sup>3</sup> Carmody, *J.A.C.S.*, 1929, **51**, 2901.

<sup>4</sup> Lucasse, *ibid.*, 1925, **47**, 743.

TABLE I.

<i>m.</i>	<i>E.</i>	<i>f.</i>	<i>E<sub>t</sub></i>	<i>E<sub>t</sub>'</i>	<i>Δ(mv).</i>	<i>T<sub>e</sub></i>
0.02	0.9814	0.685	+ 0.0388	+ 0.0387	+ 0.1	0.389
0.03	0.9680	0.647	+ 0.0335	+ 0.0335	0	0.379
0.04	0.9584	0.623	+ 0.0299	+ 0.0300	- 0.1	0.372
0.05	0.9509	0.605	+ 0.0270	+ 0.0271	- 0.1	0.366
0.06	0.9448	0.592	+ 0.0248	+ 0.0249	- 0.1	0.362
0.07	0.9396	0.580	+ 0.0230	+ 0.0230	0	0.358
0.08	0.9350	0.571	+ 0.0214	+ 0.0214	0	0.355
0.09	0.9311	0.561	+ 0.0200	+ 0.0200	0	0.352
0.10	0.9275	0.555	+ 0.0189	+ 0.0187	+ 0.2	0.349
0.20	0.9035	0.517	+ 0.0111	+ 0.0109	+ 0.2	0.331
0.30	0.8890	0.502	+ 0.0063	+ 0.0061	+ 0.2	0.320
0.40	0.8784	0.496	+ 0.0028	+ 0.0028	0	0.312
0.50	0.8703	0.490	+ 0.0001	+ 0.0002	- 0.1	0.306
0.60	0.8637	0.484	- 0.0020	- 0.0018	- 0.2	0.301
0.70	0.8577	0.485	- 0.0039	- 0.0038	- 0.1	0.297
0.80	0.8523	0.488	- 0.0055	- 0.0053	- 0.2	0.293
0.90	0.8476	0.491	- 0.0069	- 0.0067	- 0.2	0.289
1.00	0.8434	0.492	- 0.0078	- 0.0079	- 0.1	0.286
1.20	0.8363	0.493	- 0.0096	- 0.0096	0	0.261
1.40	0.8301	0.497	- 0.0110	- 0.0111	+ 0.1	0.238
1.60	0.8244	0.504	- 0.0123	- 0.0124	+ 0.1	0.216
1.80	0.8194	0.511	- 0.0134	- 0.0133	- 0.1	0.199
2.00	0.8149	0.516	- 0.0142	- 0.0143	+ 0.1	0.181
2.50	0.8042	0.535	- 0.0151			
3.00	0.7948	0.581	- 0.0150	- 0.0152	+ 0.2	- 0.059
3.50	0.7855	0.632	- 0.0145	- 0.0144	- 0.1	- 0.108
4.00	0.7774	0.682	- 0.0135	- 0.0134	- 0.1	- 0.151
4.50	0.7693	0.749	- 0.0121	- 0.0121	0	- 0.194
5.00	0.7618	0.819	- 0.0105	- 0.0103	- 0.2	- 0.233
6.00	0.7480	0.976	- 0.0068	- 0.0067	- 0.1	- 0.306
7.00	0.7339	1.206	- 0.0023	- 0.0019	- 0.4	- 0.380
8.00	0.7214	1.460	+ 0.0033	+ 0.0033	0	- 0.445
9.00	0.7098	1.754	+ 0.0081	+ 0.0088	- 0.7	- 0.507
10.00	0.6990	2.090	+ 0.0138	+ 0.0146	- 0.8	- 0.563
11.00	0.6886	2.488	+ 0.0201	+ 0.0200	+ 0.1	- 0.597
12.00	0.6784	2.973	+ 0.0260	+ 0.0264	- 0.4	- 0.597
13.00	0.6685	3.551	+ 0.0318	+ 0.0321	- 0.3	- 0.597
14.00	0.6599	4.113	+ 0.0373	+ 0.0373	0	- 0.597
15.00	0.6518	4.734	+ 0.0420	+ 0.0421	- 0.1	- 0.597
16.00	0.6448	5.323	+ 0.0458	+ 0.0463	- 0.5	- 0.597

column is given the value of  $E_t'$  obtained from the equations given below, in the sixth the deviations between columns 4 and 5, and in the seventh the transport numbers.

### The Standard Potential of the Cell.



The E.M.F. of cell (I) is given by

$$E = E^\circ - 2.3026 \frac{RT}{2F} \log a_{\text{ZnBr}_2} = E^\circ - k \log 4m^3 f_{\pm}^3 \quad (\text{A})$$

where  $E^\circ$  is the standard potential of the cell,  $E$  the observed E.M.F. and  $a_{\text{ZnBr}_2}$  the zinc bromide activity for a solution of molality  $m$ ,  $k = 2.3026 \frac{RT}{2F}$ , and  $f_{\pm}$  is the stoichiometrical activity coefficient of the salt. From the data in Table I for the six most dilute solutions,

$E^\circ$  was evaluated by the method described by Bates.<sup>5</sup> The activity coefficient  $f_{\pm}$  in the above equation may be represented by Huckel's<sup>6</sup> equation

$$-\log f_{\pm} = \frac{u\sqrt{Id}}{1 + A\sqrt{Id}} + BId,$$

where  $I$  = ionic strength =  $3m$ ,  $d$  = density of solution,  $u = 1.012$ ,  $A = 0.329 \times 10^{-8}a$ , where " $a$ " is the mean distance of approach of the ions,  $k = 2.3026 \frac{RT}{2F}$ ,  $B$  is an empirical constant. Substituting in equation (A),

$$(E^\circ + B'Id) = E + k \log 4m^3 - \frac{3ku\sqrt{Id}}{1 + A\sqrt{Id}}.$$

From the values of  $E$  and  $m$  for the first six solutions in Table I, and a value for " $a$ " of 6.2 Å. which gave the best plot, the values of  $(E^\circ + B'Id)$  in Table II were obtained.

TABLE II.

$m$ .	$E$ .	$(E^\circ + B'Id)$ .
0.02007	0.9813	0.8338
0.05071	0.9506	0.8340
0.07033	0.9394	0.8335
0.08012	0.9352	0.8337
0.09183	0.9304	0.8335
0.1120	0.9240	0.8335

TABLE III.

$m$ .	$E$ .	$(E^\circ + B'Id)$ .
0.0110	1.0698	0.9017
0.0232	1.0444	0.9018
0.0408	1.0254	0.9016
0.0792	1.0033	0.9014

Extrapolation to  $I = 0$  of a plot of  $(E^\circ + B'Id)$  against ionic strength gave  $E^\circ = 0.8339$  as the standard potential of the cell. Subtracting the value 0.0711 v. for the Ag—AgBr electrode given by Keston,<sup>7</sup> the standard potential of the Zn electrode is 0.7628 v., a value which applies both to Zn and its saturated amalgam, and which is in agreement with Bates's<sup>5</sup> recent value 0.7627 from measurements on  $\text{ZnI}_2$ , supporting it against the lower values previously recorded.

Ishikawa, Ferui and Takai<sup>8</sup> have reported measurements on the cell  $\text{Zn}_x\text{Hg}/\text{ZnBr}_2/\text{HgBr}/\text{Hg}$ . Their four most dilute solutions are given in Table III. The third column plotted against  $m$  and extrapolated to  $m = 0$  gives  $E^\circ = 0.9019$  for the cell, and accepting Bates's 0.7627 as the likeliest value for  $E^\circ_{\text{Zn}}$ , the  $\text{Hg}/\text{HgBr}/\text{Br}^-$  electrode has  $E^\circ_{\text{HgBr}} = +0.1392$ . Gerke and Geddes<sup>9</sup> obtained  $E = 0.2685$  as the mean of many determinations for the cell  $\text{H}_2/\text{HBr } 0.10015 \text{ } m/\text{HgBr}/\text{Hg}$  and using  $f_{\text{HBr } 0.1} = 0.814$ , gave  $E^\circ_{\text{HgBr}} = +0.1396$  for the mercury bromide electrode. A plot of the more recent data of Harned, Keston and Donelson<sup>10</sup> for the cell  $\text{H}_2/\text{HBr}/\text{AgBr}/\text{Ag}$ , gives  $f_{\text{HBr}} = 0.805$  at 0.10015  $m$ , and this combined with the above value for the cell gives  $E^\circ_{\text{HgBr}} = 0.1391$ , in excellent agreement with the value obtained from Ishikawa's data.

<sup>5</sup> Bates, *J.A.C.S.*, 1938, **60**, 2983.

<sup>6</sup> Huckel, *Physik. Z.*, 1925, **26**, 93.

<sup>7</sup> Keston, *J.A.C.S.*, 1935, **57**, 1671.

<sup>8</sup> Ishikawa, Ferui and Takai, *Bull. Inst. Phys. Chem. (Tokyo)*, 1936, **15**, 339.

<sup>9</sup> Gerke and Geddes, *J. Physik. Chem.*, 1927, **31**, 886.

<sup>10</sup> Harned, Keston and Donelson, *J.A.C.S.*, 1936, **58**, 89.

### The Activity Coefficients of Zinc Bromide.

The activity coefficients recorded in the third column of Table I were calculated from the equation

$$E = 0.8339 - 0.029575 \log 4m^3f^3.$$

They are plotted in Fig. 1, with those calculated from Ishikawa's data. The agreement is satisfactory up to 1 M. For the stronger solutions the more numerous results obtained in this work appear to be more accurate. The

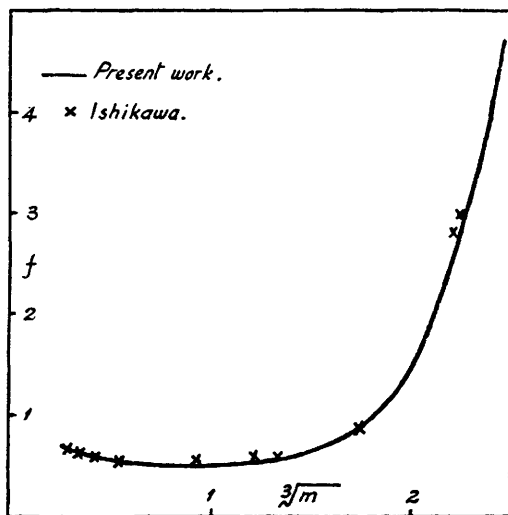


FIG. 1.

minimum activity coefficient (at about 0.6 M.) is in accordance with the behaviour of the more soluble strong electrolytes previously studied. Bates<sup>5</sup> obtained a minimum activity coefficient for zinc iodide at about 0.25 M., and for zinc chloride unpublished measurements in this laboratory give a minimum at 2.75 M. at 25° C.

The activity coefficients of the three zinc halides up to 0.1 M., are given in Table IV. For the zinc chloride results, the data of

Scatchard and Tefft<sup>11</sup> have been recalculated using  $E^\circ_{\text{Zn}} = 0.7627$ , the value accepted in this work. At the same concentration the activity coefficients are in the order  $f_{\text{ZnI}_2} > f_{\text{ZnBr}_2} > f_{\text{ZnCl}_2}$ , in agreement with that found for the sodium and potassium halides.<sup>12</sup> The data in the last column are given by the equation proposed by Davies<sup>13</sup> for univalent salts,

$$-\log f = \frac{\sqrt{I}}{1 + \sqrt{I}} - 0.2 I,$$

which holds well for calcium, barium and lead chlorides, lead and barium nitrates, and sodium sulphate. It will be seen that although the activity coefficients of  $\text{ZnCl}_2$ , which are slightly greater than those of

TABLE IV.

<i>m.</i>	$f_{\text{ZnCl}_2}$	$f_{\text{ZnBr}_2}$	$f_{\text{ZnI}_2}$	$f_{\text{Davies}}$
0.005	0.789	—	0.799	0.783
0.01	.729	—	.746	.722
0.02	.661	0.685	.690	.653
0.05	.572	.605	.621	.563
0.10	.517	.555	.578	.508

$\text{CaCl}_2$ , agree reasonably well with the equation, those of the bromide and iodide are considerably higher. This indicates that the latter

<sup>11</sup> Scatchard and Tefft, *J.A.C.S.*, 1930, **52**, 2272.

<sup>12</sup> Harned in Taylor's *Treatise on Physical Chemistry* (edn. 2), Vol. I, p. 773.

<sup>13</sup> Davies, *J.C.S.*, 1938, **141**, 2093.

salts can be regarded as completely dissociated in the concentration range considered, since incomplete dissociation would give activity coefficients lower than calculated from the equation. It suggests also that a general equation for all salts cannot be expected to hold.

### The Transport Numbers.

The E.M.F. of cell (2) is given by

$$E_t = \frac{3Rt}{2F} \cdot T_c \cdot \ln \frac{m_1 f_1}{m_2 f_2}.$$

$T_c$  is the transport number of the cation, the ion to which the electrodes are not reversible. The corresponding cell without liquid junction is a combination of two cells of type (1) and is given by

$$E = \frac{3RT}{2F} \ln \frac{m_1 f_1}{m_2 f_2}.$$

Hence  $E_t = T_c E$ , and  $T_c$  can be found. The ratio  $E_t/E$  however gives the mean transport number over the concentration range used in the cells, and to find  $T_c$  at a definite concentration, the slope of the plot of  $E_t$  against  $E$  is required. This was obtained by an analytical method, as used by MacInnes and Beattie<sup>14</sup> for lithium chloride.

It was found impossible to fit the very complex curve obtained by plotting  $E_t$  against  $E$ , by a single equation. The following four equations gave the best fit.

Between  $m = 0.02$  and  $1.0$ ,  $E_t' = 0.0158 - 0.3425E + 0.3727E^2$ , and hence by differentiation  $T_c = \frac{dE_t'}{dE} = -0.3425 + 0.7454E$ .

Between  $1\ m$  and  $2\ m$ ,  $E_t' = 1.0495 - 2.793E + 1.8255E^2$  and  $T_c = -2.793 + 3.651E$ .

Between  $3\ m$  and  $10\ m$ ,  $E_t' = 1.6952 - 4.2442E + 2.6323E^2$  and  $T_c = -4.2442 + 5.2646E$ .

Between  $11\ m$  and  $16\ m$ , the curve is linear,  $E_t' = 0.4315 - 0.5974E$ , and hence  $T_c$  is constant at  $-0.597$ .

The values of  $E_t'$  given by these equations are listed in the fifth column of Table I, with their deviations from the observed values  $E_t$  in the sixth column. The maximum deviations, and the mean deviations are as follows:  $0.02 - 2.0\ m$ , maximum  $0.2\ mv.$ , mean  $0.1\ mv.$ ;  $3.0 - 10.0\ m$ , maximum  $0.8\ mv.$ , mean  $0.25\ mv.$ ;  $11.0 - 16.0\ m$ , maximum  $0.5\ mv.$ , mean  $0.2\ mv.$  The transport number becomes negative in strong solutions. From a plot of  $\Delta E_t/\Delta m$  against  $\Delta m$ ,  $T_c$  is zero about  $2.7\ m$ .

In Fig. 2, the cation transport numbers are plotted against  $\sqrt{m}$ . The value at infinite dilution may be calculated from the mobilities of the ions. Taking  $l_{Zn^{2+}}$  at  $25^\circ C.$  as  $53.5$ , and  $l_{Br^-}$  as  $78.4$ ,<sup>15</sup>  $T_c = 0.406$  at infinite dilution. The limiting slope required by the interionic attraction theory is given by

$$\left(\frac{dT_c}{d\sqrt{c}}\right)_{c \rightarrow 0} = \frac{(Z_+ + Z_-)T_c - Z_+}{l_0} \cdot \beta\sqrt{Z_+ + Z_-},$$

<sup>14</sup> MacInnes and Beattie, *J.A.C.S.*, 1920, **42**, 1455.

<sup>15</sup> *Landolt-Bornstein Tabellen, 2er Ergänzungsband*, p. 2059.

and  $\beta$  has the value 21.14 in water at 25° C.<sup>16</sup> Taking  $l_0\text{ZnBr}_2$  as 131.9, the sum of the above limiting mobilities, the limiting slope is  $-0.218$ . This has been drawn in Fig. 2 as a straight line, and it is seen that the experimental data lie above the line, so that if accurate data were available in more dilute solutions they would probably merge into the limiting slope from above. Longworth<sup>17</sup> has shown that, if the limiting slope is negative, the transport number of strong uni-univalent electrolytes behave in this way. While lack of data below 0.02  $m$ . prevents too much stress being laid on this point, the results nevertheless support the belief derived from the activity coefficients that zinc bromide may be treated as completely dissociated at low concentrations.

At higher concentrations than 1  $m$ , the curve takes a peculiar course, the rate of decrease of  $T_c$  first falls off, then increases, being greatest

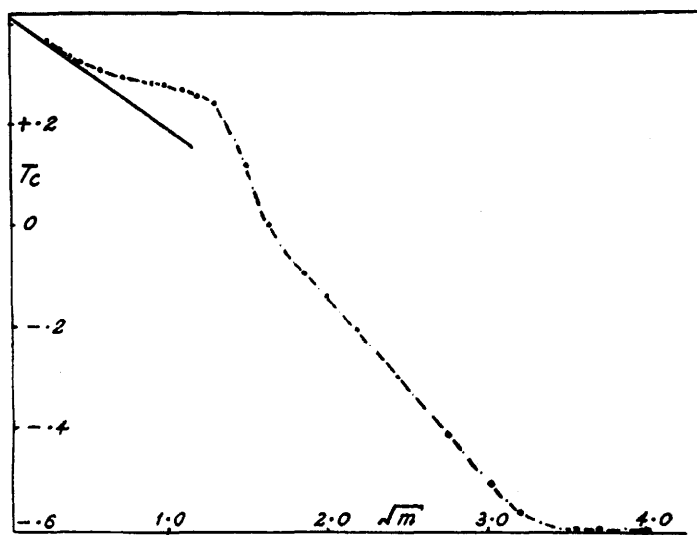


FIG. 2.

between 2  $m$  and 2.5  $m$ . It is then constant up to about 10  $m$ , and becomes zero between 10 and 11  $m$ , when the transport number becomes constant. The behaviour of  $T_c$  over the middle concentration range is presumably governed by factors such as hydration and the formation of complex anions or cations or both. No satisfactory analysis of these factors is possible. The constancy of  $T_c$  above 11  $m$ . is particularly interesting. Rabinowitsch<sup>18</sup> has reported measurements of the conductivity and viscosity of zinc bromide solutions. While the equivalent conductivity  $\Lambda$  falls with increasing concentration, the product of  $\Lambda$  and  $\eta$  (the viscosity relative to water) passes through a minimum. When the data are calculated on the molal concentration scale,  $\Lambda\eta$  gives this minimum at 13  $m$ ., with little variation between 10  $m$ . and 15  $m$ . Above 13  $m$ . then, the "corrected" conductivity increases with concentration. This change coincides roughly with the constancy of  $T_c$  and is probably governed by the same factors. It may be pointed

<sup>16</sup> Onsager and Fuoss, *J. Physic. Chem.*, 1932, **36**, 2689.

<sup>17</sup> Longworth, *J.A.C.S.*, 1935, **57**, 1185.

<sup>18</sup> Rabinowitsch, *Z. physik. Chem.*, 1921, **99**, 338.

out that a solution 9.26 molal corresponds to  $\text{ZnBr}_2 \cdot 6\text{H}_2\text{O}$ . It is possible that at this concentration the solution may have a pseudo-crystalline structure, each zinc ion being surrounded octahedrally by six water molecules, as X-ray measurements have shown to be the case in  $\text{Zn}(\text{BrO}_3)_2 \cdot 6\text{H}_2\text{O}$ , the cation unit of the crystal being  $\text{Zn}(\text{H}_2\text{O})^{++}$ . Such a view would require that the decrease in  $T_c$  found up to about 10 m. should be explained by solvation of an increasing fraction of the cations, not by the commoner assumption of the formation of complex anions such as  $\text{ZnBr}_4^{--}$ . Further addition of  $\text{ZnBr}_2$  might then dehydrate some  $\text{Zn}(\text{H}_2\text{O})^{++}$  ions, setting free  $\text{Zn}^{++}$  ions sufficient to cause a rise in the "corrected" conductivity and no further fall in  $T_c$ . If on the other hand complex anions must be postulated to explain the large negative values of  $T_c$ , the correspondence between the minimum conductivity, constant transport number, and the solution of composition  $\text{ZnBr}_2 \cdot 6\text{H}_2\text{O}$  is to be considered a coincidence. In the absence of other information, a discussion of the discrepancies in this approximate correspondence is not warranted.

### Summary.

1. Measurements are reported of cells with and without liquid junction containing aqueous solutions of zinc bromide from 0.02 m. to 16 m. at 25° C.

2. A value for the standard potential of the zinc electrode has been obtained, and the activity coefficients of zinc bromide calculated and compared with the data for similar salts.

3. The transport numbers of zinc bromide solutions have been calculated and discussed.

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