

[CONTRIBUTION FROM THE COBB CHEMICAL LABORATORY, UNIVERSITY OF VIRGINIA,  
No. 95]

## THE ACTIVITY COEFFICIENTS OF POTASSIUM CHLORIDE. AN APPLICATION OF THE EXTENDED DEBYE-HÜCKEL THEORY TO INTERPRETATION OF FREEZING POINT MEASUREMENTS

BY HUGH M. SPENCER

RECEIVED MAY 24, 1932

PUBLISHED DECEMBER 13, 1932

### Introduction

The importance of activity coefficients of potassium chloride solutions to questions of electrode potentials has made desirable a reinterpretation of the values hitherto available. The more recent values are by Scatchard<sup>1</sup> (1925, based (1) on e. m. f. measurements of MacInnes and Parker 1925, and of Beattie 1920, (2) on freezing point measurements, not corrected for heats of dilution, (3) on vapor pressure measurements of Lovelace, Frazer and Sease at 20°), Randall and White (1926, based on vapor pressure measurements of Lovelace, Frazer and Sease interpreted with the help of freezing point measurements), Jones and Bury (1927, based on their freezing point measurements, corrected for the heats of dilution)<sup>2</sup> and Harned (1929, based on e. m. f. measurements of concentration cells with intermediate amalgam electrodes).

Though the Hückel equation

$$\log \gamma = - \frac{0.356 \sqrt{2c}}{1 + A \sqrt{2c}} + 2Bc - \log(1 + 0.036m) \quad (1)$$

certainly seems to serve admirably as an empirical expression for representation of activity coefficients as a function of concentration for solutions of moderate and high concentration, the assumptions upon which the equation was derived are no longer valid at these concentrations, and in fact at lower concentrations where the assumptions are probably valid<sup>3</sup> the extended Debye-Hückel theory for symmetrical valence type salts leads to another form<sup>4</sup>

<sup>1</sup> (a) G. Scatchard, *THIS JOURNAL*, **47**, 648 (1925); (b) M. Randall and A. McL. White, *ibid.*, **48**, 2514 (1926); (c) E. R. Jones and C. R. Bury, *Phil. Mag.*, [7] **3**, 1032 (1927); (d) H. S. Harned, *THIS JOURNAL*, **51**, 416 (1929).

<sup>2</sup> Some gross error was introduced in correcting for the heat of dilution, resulting in too large corrections.

<sup>3</sup> T. H. Gronwall, V. K. La Mer and K. Sandved, *Physik. Z.*, **29**, 358 (1928).

<sup>4</sup> The first terms of Equations 1 and 2 are the same. Harned found for potassium chloride  $A = 0.76$ ,  $B = 0.0204$  and hence  $a = 3.26 \text{ \AA}$ . (This differs from the value selected in the present paper.) For 0.01 *M* KCl, by Equation 1,  $\log \gamma = 0.04528 + 0.00041 - 0.00016 = -0.04503$ ;  $\gamma = 0.9015$  and by Equation 2,  $\log \gamma = -0.04528 - 0.00057 - 0.00003 = -0.04588$ ;  $\gamma = 0.8997$ . Thus the terms added by the complete expansion of the Debye-Hückel equation have the same sign as the limiting effect term whereas the net value of the added terms of the Hückel equation has opposite sign.

$$-\log \gamma = 1.53636 \left( \frac{z^2}{10^8 a} \right) \frac{x}{1+x} - 0.15382 \left( \frac{z^2}{10^8 a} \right)^3 10^3 \left[ \frac{1}{2} X_3(x) - 2Y_3(x) \right] - 0.0770 \left( \frac{z^2}{10^8 a} \right)^5 10^5 \left[ \frac{1}{2} X_5(x) - 4Y_5(x) \right] \quad (2)$$

These factors as well as the uncertainty that the cell reactions in the amalgam cells were purely the postulated ones made it appear unwise to accept the determination made by use of Equation 1. No satisfactory calculations of the activity coefficients from freezing point measurements with corrections for the heats of dilution have been made. The partial molal heats of dilution and the partial molal heat capacities necessary for such calculations have been determined by Lange and Monheim, Wüst and Lange and by Randall and Rossini, respectively.<sup>5</sup> The freezing point determinations used include the recent ones of Karagunis, Hawkinson and Damköhler.<sup>6</sup>

These data have been treated according to the methods of Lewis and Randall and of Randall and White<sup>7</sup> with an added feature. Since the uncertainty in measurements of  $j/m^{1/2}$  rapidly becomes very large as the dilution is increased as does that of  $j/m$  for non-electrolytes,<sup>8</sup> some guiding principle besides the theoretical limit at  $m = 0$ , was sought and found in theoretical values of  $j$  calculated by Gronwall, La Mer and Sandved's<sup>3</sup> extension of the Debye-Hückel theory.

**Theoretical  $j/zm^{1/2}$  and Experimental  $j/m^{1/2}$  for Potassium Chloride.**—Values of  $j/m^{1/2}$  were calculated<sup>9</sup> for each set of experimental data and plotted as ordinate *versus*  $m^{1/2}$  as abscissas. The values from the work of Jones and Bury, Karagunis, Hawkinson and Damköhler, Adams, Hovorka and Rodebush and Menzel fall on a smooth curve mostly within the limits of error caused by the form of the function. Even though the limiting value of  $j/m^{1/2}$  be used, an undesirable amount of uncertainty remains in the course of the curve between the point where the form of the function makes its experimental value too uncertain, and infinite dilution.

<sup>5</sup> E. Lange and J. Monheim, *Z. Elektrochem.*, **35**, 29 (1929), and *Z. physik. Chem.*, [A] **150**, 349 (1930); Wüst and E. Lange, *ibid.*, **116**, 161 (1925); M. Randall and F. D. Rossini, *THIS JOURNAL*, **51**, 323 (1929). See also F. D. Rossini, *Bur. Standards J. Research*, **7**, 54 (1931).

<sup>6</sup> (a) L. H. Adams, *THIS JOURNAL*, **37**, 481 (1915); (b) F. Flügel, *Z. physik. Chem.*, **79**, 585 (1912); (c) F. Hovorka and W. H. Rodebush, *THIS JOURNAL*, **47**, 1614 (1925); (d) H. Jahn, *Z. physik. Chem.*, **50**, 144 (1904); **59**, 35 (1907); (e) E. R. Jones and C. R. Bury, *Phil. Mag.*, [7] **3**, 1032 (1927), Ref. 1c; (f) G. Karagunis, A. Hawkinson and G. Damköhler, *Z. physik. Chem.*, [A] **150**, 433 (1930); (g) H. Menzel, *Z. Elektrochem.*, **33**, 68 (1927); (h) A. D. C. Rivett, *Z. physik. Chem.*, **80**, 543 (1912); (i) W. H. Rodebush, *THIS JOURNAL*, **40**, 1204 (1918).

<sup>7</sup> (a) G. N. Lewis and M. Randall, "Thermodynamics," The McGraw-Hill Book Co., New York, 1923, p. 348; (b) M. Randall and A. McL. White, *THIS JOURNAL*, **48**, 2514 (1926).

<sup>8</sup> W. D. Harkins and R. W. Wampler, *THIS JOURNAL*, **53**, 850 (1931).

<sup>9</sup>  $j = 1 - \delta/2 \cdot 1.858m$ .

Theoretical values of  $j$ , using round values of "a" for various values of  $x (= \kappa a)$ , and thence  $j/zm^{1/2}$  as a function of  $zm^{1/2}$  for round values of "a," have been calculated from Equation 113 and Tables II, III and IV of Gronwall, La Mer and Sandved. The coefficients of the terms of the equation are different from those given by Gronwall, La Mer and Sandved, due to the use of Birge's<sup>10</sup> values of  $k = 1.3709 \times 10^{-16}$ ,  $0^\circ\text{C.} = 273.18^\circ\text{K.}$ ,  $\epsilon = 4.770 \times 10^{-10}$  and the average of Drude's and Wyman's<sup>11</sup> determinations of the dielectric constant. The change of temperature and consequently of dielectric constant is allowed for by use of three sets of coefficients shown in Table I.

TABLE I  
COEFFICIENTS OF TERMS

Range of $zm^{1/2}$	1	2	3
0 to 0.16	3.4480	0.16397	0.07798
0.16 to 0.41	3.4469	.16381	.07785
0.41 to 1.00	3.4451	.16355	.07765

For the most dilute concentrations, then

$$j = 3.4480 \frac{z^2}{10^8 a} \left[ \frac{2}{x} - \frac{1}{1+x} + \frac{2}{x^2} \ln(1+x) \right] - 0.16397 \left( \frac{z^2}{10^8 a} \right)^3 10^8 [X_3(x) - 6Y_3(x)] \\ - 0.07798 \left( \frac{z^2}{10^8 a} \right)^5 10^8 [X_5(x) - 10Y_5(x)] \quad (3)$$

The first bracket term reduces to  $2Y_1(x) - X_1(x)$ , where  $X_1(x) = 1/(1+x)$ . Values of the bracket terms were calculated, the first, from a reciprocal table and Table II, Gronwall, La Mer and Sandved, the second and third, from Tables III and IV of the same paper, respectively, for round values of "a" at various values of  $x$ .

Table II contains the values of  $j$ ,  $j/zm^{1/2}$  and  $zm^{1/2}$  resulting from Equation 3. The values of  $j/zm^{1/2}$  were plotted as ordinates against  $zm^{1/2}$  as abscissas, as in Fig. 1, with the same scales as used in plotting measured  $j/m^{1/2}$  vs.  $m^{1/2}$  for potassium chloride solutions. By superimposition of the family of the theoretical curves over the measured one, it was estimated that the parameter "a" = 3.6 Å. would coincide with the curve of measured values in the region of lowest concentrations for which the function  $j/m^{1/2}$  can be obtained with reasonable accuracy. Values of  $j$ ,  $j/zm^{1/2}$  and  $zm^{1/2}$  were calculated for this value of "a" and added to the curve of measured values. These values along with the limiting value of  $j/zm^{1/2} = 0.3726$  were used in extrapolating to infinite dilution.

The provisional values of activity coefficients,  $\gamma'$ , were determined by the method of Randall<sup>12</sup> by which

<sup>10</sup> R. T. Birge, *Rev. Modern Physics*, **1**, 1 (1929).

<sup>11</sup> (a) P. K. L. Drude, *Ann. Physik*, **59**, 61 (1896);  $D = 88.23 - 0.4044t + 0.001035t^2$ ; (b) J. Wyman, *Phys. Rev.*, **35**, 613 (1930);  $D = 78.54[1 - 0.0046(t-25) + 0.000008(t-25)^2]$ .

<sup>12</sup> M. Randall, *This Journal*, **48**, 2512 (1926).

TABLE II  
THEORETICAL VALUES OF  $j$ ,  $j/zm^{1/2}$  AND  $zm^{1/2}$

	$a$ in Å.	1	2	3	4	5	6	7	8	3.6
$x = 0.01$	$j$	0.0121932	0.0057351	0.0037919	0.0028365	0.0022665	0.0018875	0.0016172	0.0014147	0.0031537
	$j/zm^{1/2}$	.3952	.3718	.3687	.3677	.3673	.3670	.3669	.3668	.3680
	$zm^{1/2}$	.03086	.01543	.01029	.00771	.00617	.00514	.00441	.00386	.00857
$x = 0.02$	$j$	.025345	.011381	.007512	.005608	.004477	.003727	.003193	.002792	.006238
	$j/zm^{1/2}$	.4107	.3689	.3652	.3635	.3628	.3624	.3622	.3619	.3639
	$zm^{1/2}$	.06171	.03086	.02057	.01543	.01234	.01029	.00882	.00771	.01764
$x = 0.03$	$j$	.038966	.017042	.011149	.008311	.006630	.005517	.004725	.004132	.009244
	$j/zm^{1/2}$	.4210	.3687	.3613	.3591	.3581	.3576	.3573	.3571	.3595
	$zm^{1/2}$	.09256	.04628	.03086	.02314	.01851	.01543	.01322	.01157	.02571
$x = 0.04$	$j$	.052622	.022512	.014672	.010924	.008711	.007246	.006204	.005425	.012159
	$j/zm^{1/2}$	.4264	.3648	.3566	.3541	.3529	.3523	.3519	.3517	.3547
	$zm^{1/2}$	.12342	.06171	.04114	.03086	.02468	.02057	.01763	.01543	.03428
$x = 0.05$	$j$	.065298	.027847	.018117	.013478	.010743	.008935	.007649	.006688	.015013
	$j/zm^{1/2}$	.4226	.3610	.3523	.3495	.3482	.3475	.3471	.3468	.3504
	$zm^{1/2}$	.15427	.07714	.05142	.03857	.03086	.02571	.02204	.01928	.04285
$x = 0.1$	$j$	.127538	.052545	.033963	.025210	.020074	.016686	.014280	.012482	.028097
	$j/zm^{1/2}$	.4134	.3406	.3302	.3268	.3253	.3245	.3240	.3236	.3278
	$zm^{1/2}$	.3085	.1543	.1029	.0771	.0617	.0514	.0441	.0386	.0857
$x = 0.15$	$j$	.174541	.073551	.047609	.035343	.028141	.023393	.020018	.017498	.039392
	$j/zm^{1/2}$	.3771	.3178	.3086	.3055	.3040	.3033	.3028	.3025	.3064
	$zm^{1/2}$	.4268	.2314	.1543	.1157	.09256	.0771	.0661	.0579	.1286
$x = 0.2$	$j$	.208936	.091403	.059368	.044132	.035155	.029227	.025016	.021869	.049172
	$j/zm^{1/2}$	.3386	.2962	.2886	.2861	.2848	.2842	.2838	.2835	.2869
	$zm^{1/2}$	.6171	.3086	.2057	.1543	.1234	.1029	.0882	.0771	.1714
$x = 0.3$	$j$	.253181	.119348	.078275	.058332	.046524	.038717	.033151	.028988	.064958
	$j/zm^{1/2}$	.2735	.2579	.2537	.2521	.2513	.2510	.2507	.2505	.2526
	$zm^{1/2}$	.9256	.4628	.3086	.2314	.1851	.1543	.1322	.1157	.2571
$x = 0.4$	$j$	.281187	.139955	.092479	.069138	.055209	.045961	.039370	.034436	.076935
	$j/zm^{1/2}$	.2278	.2268	.2248	.2241	.2237	.2234	.2233	.2232	.2244
	$zm^{1/2}$	1.2342	.6171	.4117	.3086	.2468	.2057	.1763	.1543	.3428
$x = 0.5$	$j$	0.301863	.155393	.103317	.077408	.061877	.051544	.044165	.038637	.086080
	$j/zm^{1/2}$	.1958	.2015	.2009	.2007	.2005	.2005	.2004	.2004	.2009
	$zm^{1/2}$	1.5427	.7714	.5142	.3857	.3086	.2571	.2204	.1928	.4285
$x = 0.6$	$j$	0.318760	.167132	.111627	.083732	.067019	.055848	.047868	.041883	.093034
	$j/zm^{1/2}$	.1722	.1805	.1809	.1809	.1810	.1810	.1810	.1810	.1809
	$zm^{1/2}$	1.8513	.9256	.6171	.4628	.3703	.3086	.2645	.2314	.5142

$$\log \gamma' = -j/2.3026 - \frac{2}{2.3026} \int_0^m j/m^{1/2} dm^{1/2} + 0.000125 \int_0^m \frac{\vartheta}{m} d\vartheta \quad (4)$$

Values of  $\vartheta/m$  were plotted against  $\vartheta$  and values of the function  $0.000125 \int_0^m \vartheta/m d\vartheta$  were determined graphically for round values of concentration. These are given in Table III, along with the values of  $-\frac{j}{2.3026} - \frac{2}{2.3026} \int_0^m \frac{j}{m^{1/2}} dm^{1/2}$ ,  $\log \gamma'$  and  $\gamma'$  at round values of concentration.

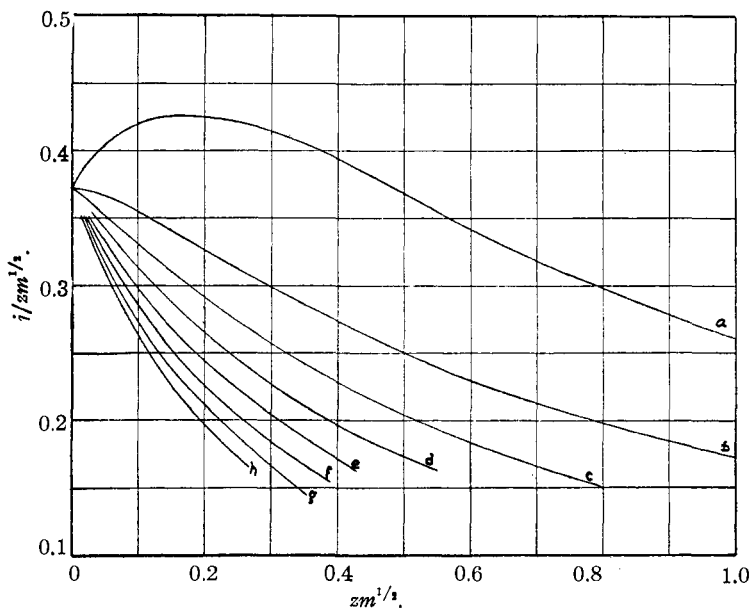


Fig. 1.—Theoretical  $j/zm^{1/2}$  vs.  $zm^{1/2}$  curves: a, 1 Å.; b, 2; c, 3; d, 4; e, 5; f, 6; g, 7; h, 8 Å.

Table IV contains the values used in the determination of the corrections due to the heat of dilution.

$$\log \gamma = \log \gamma' - 27.754 \int_0^m \frac{1}{m} dx$$

where  $x = -\bar{L}_{1(298)}y + (\bar{C}_{p1} - \bar{C}_{p1}^0)z$ ,  $y$  and  $z$  being temperature functions defined by Lewis and Randall.<sup>7a</sup> (Note other use of  $x$  and  $z$ .) The values of  $\bar{L}_1$ , the partial molal heat content of water in potassium chloride solutions at 25°, are by Lange and Monheim, those of the partial molal heat capacity for the solvent less that of pure water are by Randall and Rossini.<sup>5</sup> The values of the function  $-27.754 \int_0^m (1/m) dx$  were determined graphically and are included in Table IV along with the corrected values of  $-\log \gamma$  and  $\gamma$ .

TABLE III  
PROVISIONAL VALUES OF ACTIVITY COEFFICIENT OF POTASSIUM CHLORIDE IN AQUEOUS SOLUTIONS

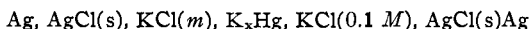
$m$	$m^{1/2}$	$-\frac{j}{2.3026}$	$-\frac{2}{2.3026} \int_0^m \frac{j/m^{1/2}}{dm^{1/2}}$	$1.25 \times 10^{-4} \int_0^m \frac{\vartheta/m}{d\vartheta}$	$\log \gamma'$	$\gamma'$
0	0	0	0		0	1
0.001	0.0316	-0.00489	-0.01000		-0.01489	0.9663
.002	.0447	- .00678	- .01402		- .02080	.9532
.005	.0707	- .01031	- .02174	0.00001	- .03204	.9289
.01	.1000	- .01392	- .03020	.00002	- .04410	.9034
.02	.1414	- .01848	- .04129	.00003	- .05974	.8715
.05	.2236	- .02586	- .06153	.00008	- .08731	.8179
.1	.3162	- .03203	- .08096	.00015	- .11284	.7712
.2	.4472	- .03836	- .10517	.00029	- .14324	.7358
.35	.5916	- .04376	- .12815	.00057	- .17134	.6740
.5	.7071	- .04720	- .14436	.00071	- .19085	.6444
.75	.8660	- .05089	- .16424	.00103	- .21410	.6108
1.0	1.0000	- .05346	- .17917	.00137	- .23126	.5871
1.25	1.1180	- .05496	- .19127	.00169	- .24454	.5695
1.5	1.2247	- .05569	- .20138	.00201	- .25506	.5559

### Discussion of Results

Gronwall, La Mer and Sandved probably had a network plot of  $j$  as a function of  $x$  for the two sets of parameters " $a$ " and  $z\kappa$  for the solution of their Equation 113. Their treatment would undoubtedly lead to satisfactory values of  $\vartheta_{(\text{obs.})} - \vartheta_{(\text{calcd.})}$ , and thus of " $a$ ," if applied in the range for which the experimental data and the assumptions underlying the theory are sufficiently accurate, and one could calculate  $\log \gamma$  in the very dilute range by Equation 2. However, if one were using the freezing point data for the determination of activity coefficients, the experimental data would be cast into the  $j/zm^{1/2}$  vs.  $m^{1/2}$  form for the range above which the assumptions of the theory are not expected to be valid, so this should prove the simpler method. The theoretical  $j/zm^{1/2}$  vs.  $zm^{1/2}$  curve can of course be used for any symmetrical valence type salt.

A plot of the function  $-27.754 \int_0^m (1/m) dx$  against molality shows that the correction for the heat of dilution lowers the activity coefficient at concentrations below about 0.12  $M$  for potassium chloride.

The data of Harned for the cell



on which his values of the activity coefficient were based have been put into the form<sup>13</sup>

$$\log \gamma + \text{const.} = - \frac{E}{0.11831} - \log m^{\pm}$$

<sup>13</sup> M. Randall, *Trans. Faraday Soc.*, **23**, 502 (1927).

TABLE IV  
CORRECTIONS DUE TO HEATS OF DILUTION AND FINAL VALUES OF THE ACTIVITY COEFFICIENTS OF POTASSIUM CHLORIDE IN AQUEOUS SOLUTIONS AT 25°

$m$	$\vartheta$	$\bar{L}_1$	$\bar{C}_{p_1} - \bar{C}_{p_1}^0$	$-y\bar{L}_1$	$+z(\bar{C}_{p_1} - \bar{C}_{p_1}^0)$	$x$	$\frac{1}{m}$	$-27.754 \int_0^m \frac{1}{m} dx$	$-\log \gamma'$	$-\log \gamma$	$\gamma$
0.001									0.01489		0.9663
.002									.02080		.9532
.005									.03204		.9289
.01	0.037	-0.0027	-0.0002	+0.00000018	-0.00000017	+0.00000001	100	-0.00006	.04410	0.04416	.9033
.02	.071	-.0061	-.0004	+.00000041	-.00000034	+.00000007	50	-.00017	.05974	.05991	.8711
.05	.171	-.0161	-.0009	+.00000109	-.00000077	+.00000032	20	-.00044	.08731	.08775	.8171
.1	.342	-.0223	-.0019	+.00000152	-.00000169	-.00000017	10	-.00026	.11284	.11310	.7707
.2	.677	+.0110	-.009	-.00000076	-.00000819	-.00000895	5	+.00148	.14324	.14176	.7383
.35	1.330	+.27	-.020	-.0000192	-.0000194	-.0000386	2.86	+.00454	.17134	.16680	.6811
.5	1.655	+.76	-.034	-.0000547	-.0000336	-.0000883	2	+.00780	.19085	.18305	.6561
.75	2.464	+2.23	-.063	-.0001658	-.0000668	-.0002326	1.33	+.01262	.21410	.20148	.6288
1.	3.265	+3.95	-.099	-.0003031	-.0001109	-.0004140	1	+.01845	.23126	.21281	.6126
1.25	4.066	+5.95	-.141	-.000471	-.0001677	-.000639	0.8	+.02407	.24454	.22047	.6019
1.5	4.866	+8.22	-.187	-.000671	-.0002340	-.000905	.667	+.02948	.25506	.22558	.5949

and plotted as abscissas against  $m^{1/2}$  as ordinate, and compared with a plot of  $\log \gamma$  vs.  $m^{1/2}$  from freezing point measurements. It is scarcely possible to superimpose as much of the first curve as that between two concentrations on the second curve. In view of the forthright thermodynamic character of the freezing point method involving, besides inaccuracy of data, only the assumption<sup>14</sup> of constancy of  $\bar{C}_{p_1} - \bar{C}_{p_1}^0$  it appears that the cell reaction is not purely the one postulated. If temperature coefficients of the cell reaction were available, a test of the purity of reaction could be made by comparison of the  $\Delta H$ 's with thermochemical values.

### Summary

1. The activity coefficients of potassium chloride in aqueous solutions at 25° have been determined from freezing point measurements including the recent ones by Jones and Bury and by Karagunis, Hawkinson and Damköhler. Corrections for the heats of dilution have been made.

2. Theoretical values of  $j$ ,  $j/zm^{1/2}$  and  $zm^{1/2}$  for symmetrical valence type salts have been calculated from the extension of the Debye-Hückel theory by Gronwall, La Mer and Sandved and offer a satisfactory guide for extrapolating from the region where the function  $j/zm^{1/2}$  becomes difficult or impossible to measure accurately, to infinite dilution.

UNIVERSITY, VIRGINIA

<sup>14</sup> Undoubtedly this assumption is not strictly valid. From the data assembled by Awbery ["International Critical Tables," Vol. V, p. 115] and Rossini's approximate equations for  $\bar{C}_{p_1} - \bar{C}_{p_1}^0$  (Ref. 5), one finds for 0.5551 *M* KCl  $-(\bar{C}_{p_1} - \bar{C}_{p_1}^0)$  at 18, 21.5 and 25° equal to 0.076, 0.065 and 0.065, for 1.110 *M* KCl, 0.155, 0.155 and 0.167, and for 1.665 *M* KCl, 0.203, 0.203 and 215 cal. mole<sup>-1</sup> deg.<sup>-1</sup>, respectively. Thus over this smaller range of temperature  $\bar{C}_{p_1} - \bar{C}_{p_1}^0$  is practically independent of the temperature, though the values at 25° do not agree with those derived without using equations by Randall and Rossini. The value of the correction is believed not to be seriously affected by this uncertainty.

Since this paper was written Saxton and Smith [THIS JOURNAL, 54, 2626 (1932)] have reported the results of their accurate measurements of the boiling points of potassium chloride solutions. They use the same values of  $\bar{C}_{p_1} - \bar{C}_{p_1}^0$  at 25° and slightly different values of  $L_1$  in correcting their activity coefficients to 100°. It is interesting to note that by assuming that  $\bar{C}_{p_2} - \bar{C}_{p_2}^0$  is also independent of temperature, they find the activity coefficients at 25° by Harned<sup>1d</sup> lead to values at 100° in good agreement with their values from boiling point measurements.