[Contribution from the Chemistry Department, University of Toronto]

The Thermodynamics of Aqueous Solutions of Calcium Chloride at Temperatures from 15–35° from E. M. F. Measurements on Cells with Transference

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The development of the concentration cell with transference as a precision method for investigating the thermodynamics of electrolytes is primarily due to MacInnes and his associates[1,2,3] at the Rockefeller Institute. While the method presupposes accurate values of the transference numbers, this is not a serious handicap thanks to the classic researches of Longsworth,[4] and measurements on such cells can under the best conditions attain a precision unobtainable by any other method. Earlier papers[5,6] from this Laboratory have extended the measurements to cover a range of temperature, and have thus made possible an independent check on the accuracy of the results through comparison of the e. m. f. measurements with the heat of dilution and heat capacity data.

The work reported here concerns calcium chloride in aqueous solution in contrast to the 1–1 salts earlier studied in this Laboratory.[5,6,7] An additional reason for selecting calcium chloride is that while isopiestic comparison of two salts at high dilutions[8] is a matter of extreme difficulty, the comparison (provided the two salts are of the same valence type) need only extend to moderately low concentrations in order to permit extrapolation of the isopiestic ratio to infinite dilution. Thus the data presented here should serve as a suitable standard for other 2–1 and 1–2 salts in aqueous solution.

The cells and the experimental technique were the same as were previously employed in the work on potassium and sodium chlorides.[5,6] In general the bias potential between the two silver–silver chloride electrodes, obtained from the initial and reversed fillings of the cell, agreed with the potential when both electrodes were in the same solution before and after the run within two or three microvolts. Similarly, duplicate measurements on the same pair of solutions with different pairs of electrodes checked one another (after correction for bias potential) within 5 microvolts as a rule. The solutions were prepared by the method of Shedlovsky and Brown[9] as described in detail by Keenan, McLeod and Gordon.[10] In computing molalities, all weights have been reduced to vacuum.

Table I

m_1	m_2	$E_{\text{obs.}}$, mv.	$E_{\text{calcd.}}$, mv.
15 °C.			
0.024908	0.0029934	+29.242	+29.245
.024973	.0060113	+19.285	+19.300
.025007	.009995	+12.257	+12.255
.024738	.015011	+ 6.603	+ 6.605
.024959	.039949	− 6.070	− 6.065
.025050	.049822	− 8.818	− 8.815
.024910	.065198	−12.283	−12.280
.024874	.074740	−14.009	−14.005
25 °C.			
0.024993	0.0033155	+29.024	+29.035
.024926	.0058595	+20.495	+20.500
.024963	.0063695	+19.310	+19.295
.025025	.009482	+13.567	+13.560
.024802	.011342	+10.883	+10.885
.024802	.014883	+ 7.050	+ 7.050
.024894	.034804	− 4.534	− 4.525
.024894	.047946	− 8.794	− 8.785
.028796	.060084	− 9.784	− 9.785
.024868	.064530	−12.709	−12.710
.025004	.074929	−14.589	−14.590
35 °C.			
0.024929	0.0030285	+31.651	+31.655
.025000	.0059720	+21.107	+21.115
.025000	.009989	+13.346	+13.335
.024914	.014983	+ 7.304	+ 7.305
.023700	.040061	− 7.372	− 7.355
.025027	.049887	− 9.607	− 9.605
.025027	.064906	−13.213	−13.210
.024929	.075054	−15.238	−15.235

The results are given in Table I as a function of the molalities m_1 and m_2 of the two solutions; in almost every case, the observed value of the e. m. f., $E_{\text{obs.}}$, is the mean of two or more measurements (see above). The electromotive force of the cell

$$\mathrm{Ag,AgCl/CaCl_2}(m_1)//\mathrm{CaCl_2}(m_2)/\mathrm{AgCl,Ag}$$

is related to the thermodynamic quantities involved by the familiar equation

$$E = k \int_{m_2}^{m_1} t_+ \, d \log \gamma m \qquad (1)$$

$$= k t_+^\circ \, \Delta \log \gamma m + k \int_{m_2}^{m_1} t_\delta \, d \log \gamma m \qquad (2)$$

where k is given by $2.3026 \times 3RT/2F$, t_+ and t_+° are the transference numbers of the cation at concentrations m and zero, respectively, $t_\delta = t_+ - t_+^\circ$, and the other symbols have their usual

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(1) A. S. Brown and D. A. MacInnes, This Journal, **57**, 1356 (1935).

(2) T. Shedlovsky and D. A. MacInnes, *ibid.*, **58**, 1970 (1936).

(3) T. Shedlovsky and D. A. MacInnes, *ibid.*, **59**, 503 (1937).

(4) L. G. Longsworth, *ibid.*, **54**, 2741 (1932); **57**, 1185 (1935).

(5) W. J. Hornibrook, G. J. Janz and A. R. Gordon, *ibid.*, **64**, 513 (1942).

(6) G. J. Janz and A. R. Gordon, *ibid.*, **65**, 218 (1943).

(7) E. A. MacWilliam and A. R. Gordon, *ibid.*, **65**, 984 (1943).

(8) A. R. Gordon, *ibid.*, **65**, 221 (1943).

(9) T. Shedlovsky and A. S. Brown, *ibid.*, **56**, 1066 (1934).

(10) A. G. Keenan, H. G. McLeod and A. R. Gordon, *J. Chem. Phys.*, **13**, 466 (1945).

significance. Equation 2 is solved for $\Delta \log \gamma$, the transference numbers of Keenan, McLeod and Gordon[10,11] being employed. As in the case of the 1–1 salts the extrapolation to zero concentration is effected by plotting $\Delta \log \gamma + \Delta(a\sqrt{m}/(1 + b\sqrt{m}))$ against m_2; here a and b are the theoretical Debye–Hückel coefficients, the latter of course involving the mean ionic radius r. If a suitable value of r has been selected, the resulting plot is linear, its slope being the coefficient D in the modified equation

$$\log \gamma = -a\sqrt{m}/(1 + b\sqrt{m}) + Dm \qquad (3)$$

Values of a and of b/r have been tabulated as a function of temperature for 1:1 salts by Manov, Bates, Hamer and Acree[12]; the corresponding coefficients for 2:1 salts may be obtained from these by multiplying by $2\sqrt{3}$ and $\sqrt{3}$ respectively. The value of r chosen for the extrapolation at all temperatures is 4.575 Å.; Table II gives the values of the coefficients involved, and the integral of equation 2 is tabulated in Table III. Table IV gives the activity coefficients, computed by equation 3 with the constants of Table II, as a function of the square root of the molality; the table also gives the osmotic coefficients, defined by

$$\varphi = 1 + (1/m)\int_0^m m\, d \ln \gamma \qquad (4)$$

TABLE II

	15°	25°	35°
k, mv.	85.731	88.707	91.682
t_+°	0.4334	0.4380	0.4427
a	1.7321	1.7615	1.7925
b	2.588	2.600	2.613
D	0.198	0.203	0.185

TABLE III

$$-k\int_0^m t_3\, d \log \gamma m$$

$m^{1/2}$	15°	25°	35°
0.04	0.418	0.434	0.447
.08	0.814	0.841	0.868
.12	1.194	1.234	1.273
.16	1.565	1.616	1.667
.20	1.926	1.988	2.049
.24	2.277	2.350	2.419
.28	2.619	2.702	2.782

TABLE IV

	15°		25°		35°	
$m^{1/2}$	$1 + \log \gamma$	φ	$1 + \log \gamma$	φ	$1 + \log \gamma$	φ
0.04	0.9375	0.9545	0.9365	0.9538	0.9354	0.9530
.08	.8865	.9215	.8846	.9203	.8826	.9188
.12	.8442	.8975	.8418	.8960	.8389	.8940
.16	.8091	.8805	.8061	.8788	.8025	.8763
.20	.7797	.8687	.7763	.8669	.7719	.8640
.24	.7550	.8612	.7514	.8594	.7463	.8560
.28	.7343	.8571	.7305	.8554	.7247	.8514

That equation 3 gives an adequate representation of the activity coefficients is shown by the column headed $E_{\text{calcd.}}$ in Table I, which gives the e. m. f. computed by interpolation using mean second differences from Tables III and IV. It is apparent that the agreement is satisfactory; in only five instances is the discrepancy between calculated and observed greater than 0.01 mv.

Calcium chloride concentration cells with transference have been studied by Shedlovsky and MacInnes[3] at 25°. That our measurements are in good agreement with theirs is evident from the accompanying table; the first line gives their observed e. m. f. for the five cells involving concentrations up to 0.05 mole per liter, while the second gives the e. m. f. computed from Tables III and IV after converting to molal concentrations; in only one instance does the discrepancy correspond to more than 0.0002 in $\Delta \log \gamma$.

$E_{\text{obs.}}$, S. and MacI.	47.545	29.263	22.697	9.751	3.819
$E_{\text{calcd.}}$	47.540	29.260	22.675	9.750	3.810

On the other hand, the activity coefficients they report, owing to the different transference numbers they employ, differ considerably from those listed in Table IV, *e. g.*, for 0.05 *m*, their equation 8a predicts $\gamma = 0.5835$, while interpolation in Table IV gives $\gamma = 0.5769$. It should also be noted that if equation 3 be assumed valid up to 0.1 *m*, it predicts $\gamma = 0.518$ for this concentration at 25°. This differs radically from the value computed by Robinson[13] from freezing point measurements *viz.*, 0.531. While such measurements can give reliable activity coefficients near the freezing point, values computed from them for moderate concentrations and much higher temperatures must always be suspect in the absence of fairly complete heat of dilution and heat capacity data.

With the 1:1 salts[5,6,7] it was possible to show that the measurements on cells with transference at low concentrations were consistent with those on cells without transference at higher concentrations; in fact, extrapolation of the equations corresponding to (3) predicted the e. m. f. for cells without transference within experimental precision up to two or three tenths molal. A similar comparison here is much more ambiguous. Scatchard and Tefft[14] employed cells with calcium amalgam electrodes for concentrations down to 0.01 *m*. If equation 3 be assumed valid up to 0.1 *m*, their reference concentration, it predicts Scatchard and Tefft's results more closely[15] than the equation they employ for the activity

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[11] For a discussion of the transference numbers used here and the earlier 25° data of Longsworth (ref. 4) see ref. 10.

[12] G. G. Manov, R. G. Bates, W. J. Hmaer and S. F. Acree, THIS JOURNAL, 65, 1765 (1943).

[13] R. A. Robinson, *Trans. Faraday Soc.*, 36, 735 (1940).

[14] G. Scatchard and R. F. Tefft, THIS JOURNAL, 52, 2265, 2272 (1930).

[15] Scatchard and Tefft's observed e. m. f. for the five cells they report in the range 0.01 *m* – 0.1 *m* are 76.1, 74.2, 43.9, 41.2 and 28.92 mv.; the corresponding calculated values are 75.9, 73.9, 44.1, 41.9 and 28.89 mv. For the last cell, the discrepancy corresponds to about 0.08% in γ, and for the first to about 0.5%.

coefficients; moreover, as might be expected, the agreement is closest for the cell with highest concentration. On the other hand, Robinson's isopiestic measurements[13] have raised some doubt as to whether such cells are truly reversible.

Even in the absence of complete heat capacity data (see below), it is nevertheless possible to obtain an independent check on the accuracy of our results by means of the relation

$$\partial \ln \gamma/\partial T = -\bar{L}_2/3RT^2 \qquad (5)$$

In Fig. 1, the circles indicate the values of $\bar{L}_2$ at 25° obtained from tabular differentiation with respect to temperature of the entries in Table IV.

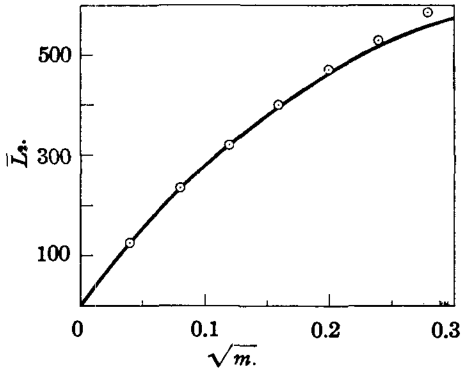

Fig. 1.

The continuous curve gives Lange and Streeck's calorimetric[16] values of $\bar{L}_2$ as recalculated by Harned and Owen.[17] When it is remembered that the radius of the circles in the figure, *viz.*, 12 calories per mole, corresponds for the cells studied here to an uncertainty of approximately 0.4 microvolt per degree, it is apparent that the agreement is well within the precision of the e. m. f. measurements except for the highest concentration where the discrepancy is approximately 30 calories per mole.

A plot of the apparent molal heat capacity, computed from Richards and Dole's 20° data,[18] is linear in $\sqrt{m}$ at concentrations less than tenth molar; the slope of the plot corresponds to a $\bar{J}_2 = \bar{C}_{p_2} - \bar{C}^0_{p_2}$ of approximately $75\sqrt{m}$. If this be assumed valid for the range 15 – 25° it is then possible from the calorimetric values of $\bar{L}_2$ and $\bar{J}_2$ to compute the 15° entries in Table IV from those for 25° by integration of equation 5. The values so obtained agree with those entered in the table within 0.0001 or better in log γ except for 0.0256 *m* where the discrepancy is 0.0002. While the test of the e. m. f. measurements by means of the thermal data cannot be as rigorous here as in the case of potassium chloride[5] and of sodium chloride,[6] we nevertheless believe that it provides reasonably satisfactory evidence[19] for the accuracy of our results.

Summary

1. The e. m. f. of the cell with transference Ag, AgCl/$CaCl_2(m_1)$//$CaCl_2(m_2)$/AgCl, Ag has been measured for concentrations from 0.003 to 0.075 *m* at temperatures from 15–35°. Activity and osmotic coefficients are tabulated for these ranges of concentration and temperature.

2. The results for 25° are in good agreement with the measurements of Shedlovsky and MacInnes for this temperature. The activity coefficients reported here differ appreciably from those given by Shedlovsky and MacInnes owing to the different transference numbers employed in interpreting the data in the two researches.

3. The variation of the activity coefficient with temperature is consistent with the existing heat of dilution and heat capacity data.

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[16] E. Lange and H. Streeck, *Z. physik. Chem.*, **152A**, 1 (1931).

[17] H. S. Harned and B. B. Owen, "The Physical Chemistry of Electrolytic Solutions," 1943, p. 541, Table (8-2-2A).

[18] T. W. Richards and M. Dole, This Journal, **51**, 794 (1929).

[19] If a mean value of $\bar{J}_2 = 100\sqrt{m}$ be assumed for the range 25–35°, a calculation similar to that discussed yields values of log γ for 35° agreeing with the table as printed within one or two units in the fourth decimal place except for 0.0784 *m*, where the discrepancy is 0.0003. The value assumed for $\bar{J}_2$ for this interval is not unreasonable, although it corresponds to a more rapid increase in $\bar{J}_2$ with temperature than has been found from e. m. f. measurements on other 2:1 salts; see Harned and Owen (ref. 17) p. 572 Table (13-3-4A).