Thermodynamics of Concentrated Electrolyte Mixtures. 5. A Review of the Thermodynamic Properties of Aqueous Calcium Chloride in the Temperature Range 273.15–373.15 K

J. Ananthaswamy[†] and Gordon Atkinson*

Department of Chemistry, University of Oklahoma, Norman, Oklahoma 73019

A complete review of the thermodynamic properties of aqueous CaCl₂ solutions has been carried out. The temperature range covered was 0–100 °C and the concentration range 0–9.0 *m*. The complete data set was fitted to appropriate Pitzer equations as modified for CaCl₂ by Rogers. The derived parameters for osmotic coefficients, activity coefficients, apparent molal enthalpies, and apparent molal heat capacities are given. The fit is compared with the original data and the earlier fit of Phutela and Pitzer.

Calcium chloride is a major constituent of natural waters and is important in many biological and industrial fluids. In addition, aqueous calcium chloride is used as an isopiestic standard. Therefore, an accurate knowledge of the thermodynamic properties of aqueous calcium chloride over a wide temperature range is desirable. The osmotic and activity coefficients of aqueous calcium chloride at 25 °C were reviewed and summarized by Robinson and Stokes (1) and more recently by Staples and Nuttall (2) and Rard, Habenschuss, and Spedding (3). After the completion of this work we received a paper by Pitzer (4) which describes the thermodynamic properties of calcium chloride up to about 4.0 *m*. But expressions for thermodynamic properties of calcium chloride over a wide temperature range up to saturation solubility are still lacking. In the present work we have reviewed all the available osmotic coefficients, activity coefficients, apparent molal heat capacities, apparent molal enthalpies, and differential heats of dilution of calcium chloride in the temperature range of 0–100 °C. Vapor pressure data were corrected for the nonideal behavior of water vapor. After the necessary corrections, the data were fitted to the virial expressions developed by Rogers (5).

Data Treatment

The activity and osmotic coefficient data for aqueous CaCl₂ solutions at 25 °C were taken from the work of Rard, Habenschuss, and Spedding (3).

McLeod and Gordon (6) measured the emf's of concentration cells with transference and corrected the results for the transference numbers of the cation. The activity coefficients of aqueous CaCl₂ solutions at the experimental molalities were calculated at 15 and 35 °C. The values are listed in Table I.

Mussini and Pagella (7) measured the emf's of the calcium amalgam electrode at 40, 55, and 70 °C and listed the activity coefficients of aqueous CaCl₂ solutions at rounded molalities. The activity coefficients at the experimental molalities were calculated and are given in Table I.

Jakli and Van Hook (8) reported the osmotic coefficients of aqueous CaCl₂ solutions between 0 and 90 °C. For solutions of concentration 5.4185 and 7.8767 *m* smoothed data sets were used, and for 2.9573 *m* solutions the basic data as reported were used. They corrected their data for the nonideal behavior of water vapor. Therefore, their data were used

without further treatment. Similarly, the osmotic coefficients of calcium chloride at 0 °C reported by Platford (9), and at 15 °C reported by Childs and Platford (10), were used as reported.

Bechtold and Newton (11) measured the vapor pressures of 3.0335 and 7.0310 *m* CaCl₂ solutions at 35 °C and 0.3043, 3.0335, and 7.0310 *m* CaCl₂ solutions at 45 °C. Their data were corrected for the nonideal behavior of the solvent vapor by using *B* values (12) of −989.4 and −852.3 cm³ mol⁻¹ at 35 and 45 °C, respectively. The resulting osmotic coefficients are listed in Table I.

Hakuta, Goto, and Ishizaka (13) and Plake (14) measured the boiling point elevation of aqueous CaCl₂ solutions up to 1.64 and 0.32 *m*, respectively. These boiling point elevation values were substituted in the equation given by Smith (15) and the resulting osmotic coefficients are listed in Table I.

Recently, Holmes, Baes, and Mesmer (16) measured the osmotic coefficients of aqueous CaCl₂ solutions in the temperature range 382–474 K. As the present fit is for the range of 0–100 °C, only their data at 382 and 413.8 K were used in order to make the present fit continuous with the high-temperature data. Their osmotic molalities were converted into osmotic coefficients after calculating the osmotic coefficients of the sodium chloride solutions by using the equation given by Silvester and Pitzer (17). The osmotic coefficients of aqueous CaCl₂ solutions thus calculated are listed in Table I.

The relative apparent molal enthalpies at 25 °C over the concentration range 0.000 11–6.5 *m* were calculated from the latest fit worked out by Parker, Garvin, and Staples (18) at the National Bureau of Standards, Washington, DC, and the values are listed in Table II. This new fit reproduces the experimental data in the 1 *m* concentration region better than the earlier data of Parker, Wagman, and Evans (19). Leung and Millero (20) measured the enthalpies of dilution of aqueous CaCl₂ solutions at 30 °C. The relative apparent molal enthalpies (^φL) at the experimental molalities were calculated by using the *B* and *C* parameters given by the authors (20) and the values are listed in Table II.

Perachon and Thourey (21) measured the enthalpies of dilution of aqueous CaCl₂ solutions at 25 °C up to a concentration of 3 *m*. The apparent molal enthalpies reported by them (21) were used without further treatment.

Lilich, Chernykh, and Rumyantseva (22) measured the heats of dilution of aqueous CaCl₂ solutions at 0 °C (up to a concentration of 5.4 *m*) and 50 °C (up to a concentration of 11.9 *m*). The relative apparent molal enthalpies calculated from their data are listed in Table II.

Richards and Dole (23) measured the heats of dilution of aqueous CaCl₂ solutions at 20 and 25 °C. Their data at 25 °C were taken into consideration by Parker et al. (18) in obtaining the ^φL fit at 25 °C. Therefore, only their data at 20 °C were used in the present fit and are listed in Table II.

Tucker (24) measured the heats of dilution of aqueous CaCl₂ solutions in the temperature range of 14–18 °C. Their data set was not included in the present fit because it was included in the fit by Parker, Garvin, and Staples (18). Hunter and Bliss (25) indirectly estimated the heats of dilution of aqueous CaCl₂

Table I. Activity and Osmotic Coefficients of Aqueous Calcium Chloride Solutions

McLeod and Gordon (6)—Concentration Cells

15 °C		35 °C	
$m/(\text{mol kg}^{-1})$	$\gamma_{\pm}$	$m/(\text{mol kg}^{-1})$	$\gamma_{\pm}$
0.002 993 4	0.8271	0.003 028 5	0.8210
0.006 011 3	0.7751	0.055 972 0	0.7689
0.009 995 0	0.7318	0.009 989 0	0.7241
0.015 011	0.6948	0.014 983	0.6863
0.039 949	0.6022	0.049 887	0.5707
0.049 82	0.5818	0.064 906	0.5468
0.065 198	0.5580	0.075 054	0.5342
0.074 74	0.5464		

Mussini and Pagella (7)—Calcium
Amalgam Electrode

	$\gamma_{\pm}$		
$m/(\text{mol kg}^{-1})$	40 °C	55 °C	70 °C
0.005 828		0.7609	
0.009 197	0.7275	0.7193	0.7119
0.014 72		0.6730	0.6645
0.019 32	0.6561		0.6361
0.029 15	0.6155	0.6029	0.5924
0.034 03		0.5869	
0.038 83		0.5733	
0.048 30	0.5668	0.5511	0.5391[a]
0.058 48		0.5318[a]	0.5191[a]
0.072 36	0.5296		0.4970[a]
0.096 80	0.5036	0.4807[a]	0.4663[a]

Bechtold and Newton (11)—Vapor
Pressure Data

	ϕ	
$m/(\text{mol kg}^{-1})$	35 °C	45 °C
0.3043		0.7901[a]
3.0335	1.7601	1.7293
7.0310	2.9530	2.8290

Hakuta, Goto, and Ishizaka (13)—Boiling Point Elevation
Data

$m/(\text{mol kg}^{-1})$	ϕ	$m/(\text{mol kg}^{-1})$	ϕ	$m/(\text{mol kg}^{-1})$	ϕ
0.095 15	0.7509[a]	0.5877	0.8184[a]	1.102	0.9637[a]
0.1922	0.7500[a]	0.6872	0.8429[a]	1.198	0.9874[a]
0.3008	0.7768[a]	0.7972	0.8585[a]	1.326	0.9952[a]
0.3754	0.7985[a]	0.8759	0.8920[a]	1.496	1.038[a]
0.4893	0.7913[a]	1.005	0.9236[a]	1.643	1.056[a]

Plake (14)—Boiling Point Elevation Data

$m/(\text{mol kg}^{-1})$	ϕ	$m/(\text{mol kg}^{-1})$	ϕ	$m/(\text{mol kg}^{-1})$	ϕ
8.090×10^{-4}	0.9959[a]	6.470×10^{-3}	0.9129	0.0650	0.8075
1.620×10^{-3}	0.9546	0.0158	0.8800	0.1600	0.7995
3.240×10^{-3}	0.9385	0.0327	0.8503	0.315	0.8467[a]

Holmes, Baes, and Mesmer (16)—Isopiestic Data

382.0 K		413.8 K	
$m/(\text{mol kg}^{-1})$	ϕ	$m/(\text{mol kg}^{-1})$	ϕ
3.2485	1.535	3.2289	1.392
3.2388	1.537	3.1048	1.365
3.2282	1.538	3.1001	1.363
3.2174	1.534	2.9253	1.322
3.2073	1.526	2.8926	1.314
3.177	1.521	2.8914	1.314
2.8979	1.448	2.5056	1.224
2.8874	1.445	2.5067	1.223
2.8757	1.440	2.4098	1.202
2.8633	1.438	2.1300	1.137
2.8499	1.434	1.8449	1.073
2.4949	1.335	1.8039	1.064
2.4841	1.334	1.4274	0.9820
2.0316	1.212	1.4054	0.9771
2.0219	1.208	1.3856	0.9732
1.6534	1.112	0.8799	0.8759
1.6525	1.112	0.8791	0.8750
1.1898	1.002	0.8313	0.8691
1.0641	0.9715	0.8237	0.8684
0.9846	0.9491		
0.8028	0.9100		
0.8012	0.9099		

[a] Indicates that these data points were given zero weight in the final least-squares fit.

solutions from the directly measured latent heats of vaporization. Their data were not included in the present fit because of the large internal deviations (as high as ±40%) in the data.

The apparent molal heat capacities ($^{\phi}C_p$) at 25 °C reported by Perron, Desnoyers and Millero (26) were corrected by multiplying with 1.020 as suggested by Desnoyers, de Visser, Perron and Picker (27). The $^{\phi}C_p$ values at 25 °C reported by Perron, Roux, and Desnoyers (28) and Spitzer, Singh, McCurdy, and Hepler (29) were used without modification.

The specific heat at 25 °C of aqueous calcium chloride solutions measured by Vasilev, Fedyainov, and Kurenkov (30), Fedyainov, Vasilev, and Karapet'yants (31), and Karapet'yants, Vasilev, and Fedyainov (32) were converted to $^{\phi}C_p$ by taking the specific heat of pure water at 25 °C as 4.1793 J and the mechanical equivalent of heat (J) equal to 4.184 J/cal and the results are tabulated in Table II. Similarly, the specific heats at 25, 50, and 75 °C measured by Rutskov (33) were converted to $^{\phi}C_p$. At each of these temperatures only the high-concentration data of Rutskov (33) were used (listed in Table II) because the low-concentration data do not agree well with the recent measurements of Gates, White, and Wood (34) and

the other data at 25 °C (26–32). Specific heats of pure water were taken as 4.1807 and 4.1928 J g^{-1} K^{-1} at 50 and 75 °C, respectively. Varasova, Mischenko, and Frost (46) measured the specific heat of the saturated solution of aqueous $CaCl_2$ at 25 °C which was converted to $^{\phi}C_p$ and listed in Table II.

Gates, White, and Wood (34) measured the specific heats and then calculated the apparent molal heat capacities of aqueous $CaCl_2$ solutions over the temperature and concentration ranges of 33–330 °C and 0.0507–3.0284 m, respectively, at a pressure of about 175 bar. Their data up to 178 °C were corrected to 1-atm pressure by using the relation

$$(^{\phi}C_p)_{p_2} - (^{\phi}C_p)_{p_1} = -T \int_{p_1}^{p_2} \left(\frac{\partial^2 \phi_v}{\partial T^2} \right)_p dp$$

$$= - \int_{p_1}^{p_2} \left(\frac{\partial \phi_E}{\partial T} \right)_p dp$$

Recently Thomas, Atkinson, and Atkinson (35) have expressed

Table II. Thermal Properties of Aqueous Calcium Chloride Solutions

$m/$ (mol kg^{-1})	$\phi L/$ (J mol^{-1})	$m/$ (mol kg^{-1})	$\phi L/$ (J mol^{-1})	$m/$ (mol kg^{-1})	$\phi L/$ (J mol^{-1})
Parker, Garvin, Staples (18) 25 °C		Leung and Millero (20) 30 °C		Lilich, Chernykh, and Rumyantseva (22) 0 °C	
6.5	16897	0.98994	4545.0	5.4	5084[a]
6.0	15371	0.69652	3994.2	5.0	4310[a]
5.5509	12536	0.5904	3813.9	4.0	2845[a]
4.6257	11343	0.50506	3644.8	3.0	1862
4.2699	10371	0.39396	3400.9	2.0	1213[a]
3.7006	8903.9	0.32063	3213.7	1.0	648.5[a]
2.7754	6797.4	0.18961	2770.3	0.6	418.4[a]
2.2203	5721.6	Perachon and Thourey (21) 25 °C		0.2	230.1[a]
1.3877	4373.7			50 °C	
1.1102	3980.3	3.00	7903.6	11.9	43.22
0.74012	3462.8	1.00	3962.2	11.0	40.17
0.55509	3181.3	0.48	3472.7	10.5	38.53
0.18503	2349.8	0.245	2891.1[a]	9.5	35.10
0.13877	2161.2	0.133	2518.8[a]	9.0	33.43
0.11102	2020.3	0.048	782.4[a]	8.5	31.80
0.05551	1738.8	0.025	175.7[a]	8.0	30.21
0.06939	1612.8			7.5	28.66
0.02775	1256.6			7.0	27.07
0.01110	873.6			6.0	23.89
5.5509 × 10^{-3}	650.1			5.0	20.54
2.7754 × 10^{-3}	477.2			4.0	17.45[a]
1.1102 × 10^{-3}	312.3			3.0	14.94[a]
5.5509 × 10^{-4}	224.8			2.0	12.59[a]
1.1102 × 10^{-4}	103.0			1.0	8.080[a]
				0.6	5.648
				0.2	3.975
				Richard and Dole (23) 20 °C	
				1.1102	3405.5
				0.55508	2769.1
				0.27754	2295.0
				0.13877	1901.3
				0.069385	1550.7
				0.034693	1235.2

$m/$ (mol kg^{-1})	$\phi C_p/$ (J K^{-1} mol^{-1})	$m/$ (mol kg^{-1})	$\phi C_p/$ (J K^{-1} mol^{-1})	$m/$ (mol kg^{-1})	$\phi C_p/$ (J K^{-1} mol^{-1})
Vasilev, Fedyainov, and Kurenkov (30) 25 °C		Fedyainov, Vasilev, and Karapet'yants (31) 25 °C		Karapet'yants, Vasilev, and Fedyainov (32)	
0.5177	-218.8[a]	1.4076	-157.1		
1.0081	-182.6	2.7225	-102.2	0.754	-182.4
1.8427	-135.3	3.8442	-57.99	1.234	-167.5
2.6809	-100.7	4.3258	-41.60[a]	1.742	-131.7
3.7899	-59.94	4.7160	-27.54	2.161	-120.9
5.1042	-15.08[a]	5.5203	-4.012[a]	2.505	-109.2
5.6803	0.7972[a]			2.756	-100.9

sample no.	temp/ °C	$m/$ (mol kg^{-1})	$\phi C_p/$ (J K^{-1} mol^{-1})
Rutskov (33)			
1	25	0.5552	-203.2
2	25	1.001	-176.4
3	25	1.1102	-168.5
4	25	1.5416	-150.8
5	25	2.2202	-125.4
6	25	3.0829	-85.52
7	25	4.6249	-30.61
8	25	6.9396	14.66
9	50	6.9396	25.71
10	50	9.2509	38.06
11	50	11.101	44.91
12	75	6.9396	36.24
13	75	9.2509	49.13
14	75	11.101	51.39
Varasova, Mischenko, and Frost (46)			
1	25	7.333	10.90[a]
Gates, White, and Wood (34)			
1	33.06	0.0507	-210.22
2	33.06	0.1011	-201.87
3	33.06	0.2509	-186.93
4	33.06	0.5017	-171.06
5	33.06	1.0049	-143.72
6	33.06	1.0049	-143.72
7	33.06	2.0040	-103.36
8	33.06	3.0284	-66.56
9	34.02	3.0284	-68.14
10	51.24	0.0507	-200.75
11	51.24	0.1011	-193.49
12	51.24	0.2509	-173.92
13	51.24	0.5017	-158.65
14	51.24	1.0049	-131.72
15	51.24	2.0040	-90.63
16	76.91	0.1011	-190.35
17	76.91	0.2409	-168.45
18	76.91	0.5017	-150.91
19	76.91	1.0049	-120.51
20	76.91	2.0040	-77.00
21	76.71	0.05070	-211.42
22	76.71	0.05070	-211.42
23	76.71	0.1011	-183.83
24	76.71	0.2509	-172.18
25	76.71	0.5017	-151.20
26	76.71	1.0049	-123.96
27	130.80	0.0507	-274.06
28	130.80	0.1011	-247.18
29	130.80	0.2509	-211.47
30	178.03	0.0507	-311.17
31	178.03	0.1011	-269.35
32	178.03	0.2509	-262.67
33	178.03	0.5017	-212.71
34	178.03	1.0049	-152.45
Saluja (36)			
1	75	0.98452	-117.65
2	75	0.49449	-149.10
3	75	0.20271	-163.85
4	75	0.10046	-187.77
5	75	0.10015	-183.51
6	75	0.05108	-204.01
7	75	0.04975	-207.43
8	75	0.02079	-210.65
9	75	0.02073	-213.92
10	100	0.4699	-173.80
11	100	0.2106	-193.65
12	100	0.07520	-221.53

[a] Indicates that these data points were given zero weight in the final least-squares fit.

Table III. Apparent Molal Heat Capacities at Zero Concentration ($\bar{C}_{p_2}°$) of Aqueous Calcium Chloride Solutions

temp/°C	$\tilde{C}_{p_2}°$/(J K^{-1} mol^{-1})	ref
20	−304.3	23, 45
25	−275.7	47
33.06	−237.6	34
51.24	−235.9	34
75.00	−249.8	36
76.71	−250.0	34
130.8	−344.3	34
178.0	−435.9	34

Table IV. Least-Squares Fitting Parameters for Aqueous CaCl$_2$

q_1	3.39701×10^{-1}
q_2	5.10778×10^{3}
q_3	4.64785×10^{1}
q_4	-1.38971×10^{-1}
q_5	6.82557×10^{-5}
q_6	1.50481
q_7	-4.98241×10^{2}
q_8	0.0
q_9	-1.64685×10^{-2}
q_{10}	2.34630×10^{-5}
q_{11}	-2.67882×10^{-2}
q_{12}	-9.67633×10^{3}
q_{13}	-8.48338×10^{1}
q_{14}	2.46219×10^{-1}
q_{15}	-1.18352×10^{-4}
q_{16}	8.41344×10^{-3}
q_{17}	3.83610×10^{3}
q_{18}	3.39226×10^{1}
q_{19}	-9.95956×10^{-2}
q_{20}	4.84995×10^{-5}
q_{21}	-9.36925×10^{-4}
q_{22}	-5.65554×10^{2}
q_{23}	-5.04325
q_{24}	1.49455×10^{-2}
q_{25}	-7.35441×10^{-6}
q_{26}	3.04100×10^{-5}
q_{27}	2.76926×10^{1}
q_{28}	2.48007×10^{-1}
q_{29}	-7.38508×10^{-4}
q_{30}	3.65452×10^{-7}
q_{31}	-2.75690×10^{2}
q_{32}	2.73117
q_{33}	-4.99191×10^{-2}
q_{34}	1.65270×10^{-4}

the $(\partial\phi_E)/\partial T)_p$ for aqueous CaCl$_2$ solutions as

$$(\partial\phi_E/\partial T)_p = -0.004437 + 0.001353M^{1/2}$$

These two equations were combined to get

$$(^\phi C_p)_{p_2} =$$
$$(^\phi C_p)_{p_1} - 0.1T(-0.004437 + 0.001353M^{1/2})(p_2 - p_1)$$

The factor 0.1 was added because 1 cm^3 bar = 0.1 J. The final values obtained after the pressure correction and used in the present fit are listed in Table II.

Saluja (36) measured the heat capacities of aqueous CaCl$_2$ solutions at 75 and 100 °C at a pressure of 0.6 MPa. The pressure correction to convert his data to 1 atm was negligible and hence the data were used as such and are listed in Table II.

The Koch (37) data set on the specific heats of aqueous CaCl$_2$ were not included in the present fit because it lacks internal consistency at several temperatures (0–30 °C). The apparent molal heat capacities at lower temperatures have an opposite slope to that established by the data of other workers.

Similarly, the specific heats measured by Dickinson, Mueller, and George were not included in the present fit because (i) they reported only the densities of the experimental solutions rather than the molalities and (ii) their data at 20 °C have the same inconsistency as was pointed out in case of the Koch (37) data.

The differential heats of dilution (ΔH_D) at 40, 50, 60, 70, and 80 °C reported by Harrison and Perman (39) were converted into the relative partial molal enthalpies of the solvent by using the relation

$$\bar{L}_1 = 18.0152\Delta H_D$$

and then used in the least-squares fit.

General Equations

The basic equations, of thermodynamic properties as a function of concentration, used in the present work were derived by Rogers (5) and are an extension of the ion–interaction formalism introduced by Pitzer and co-workers (40–43). These equations are summarized as follows:

$$\phi - 1 = |Z_M Z_X|f^\phi + 2\left(\frac{\nu_M \nu_X}{\nu}\right)mB_{MX}^\phi + \frac{2(\nu_M \nu_X)^{3/2}}{\nu}m^2 C_{MX}^\phi$$
$$+ \frac{2(\nu_M \nu_X)^2}{\nu}m^3 D_{MX}^\phi + \frac{2(\nu_M \nu_X)^{5/2}}{\nu}m^4 E_{MX}^\phi + \frac{2(\nu_M \nu_X)^3}{\nu}m^5 F_{MX}^\phi \quad (1)$$

$$\ln \gamma_{MX} = |Z_M Z_X|f^\gamma + \frac{2(\nu_M \nu_X)}{\nu}mB_{MX}^\gamma +$$
$$\frac{3(\nu_M \nu_X)^{3/2}}{\nu}m^2 C_{MX}^\phi + \frac{8}{3}\frac{(\nu_M \nu_X)^2}{\nu}m^3 D_{MX}^\phi +$$
$$\frac{10}{4}\frac{(\nu_M \nu_X)^{5/2}}{\nu}m^4 E_{MX}^\phi + \frac{12}{5}\frac{(\nu_M \nu_X)^3}{\nu}m^5 F_{MX}^\phi \quad (2)$$

$$^\phi L = \nu|Z_M Z_X|A_H[1/2b] \ln(1 + bI^{1/2}) -$$
$$2(\nu_M \nu_X)RT^2 mB_{MX}^L - (\nu_M \nu_X)^{3/2}RT^2 m^2 C_{MX}^L -$$
$$\frac{2}{3}(\nu_M \nu_X)^2 RT^2 m^3 D_{MX}^L - \frac{1}{2}(\nu_M \nu_X)^{5/2}RT^2 m^4 E_{MX}^L -$$
$$\frac{2}{5}(\nu_M \nu_X)^3 RT^2 m^5 F_{MX}^L \quad (3)$$

$$^\phi C_p = \bar{C}_{p_2}° + \nu|Z_M Z_X|A_J[1/2b] \ln(1 + bI^{1/2}) -$$
$$2(\nu_M \nu_X)RT^2 mB_{MX}^J - (\nu_M \nu_X)^{3/2}RT^2 m^2 C_{MX}^J -$$
$$\frac{2}{3}(\nu_M \nu_X)^2 RT^2 m^3 D_{MX}^J - \frac{1}{2}(\nu_M \nu_X)^{5/2}RT^2 m^4 E_{MX}^J -$$
$$\frac{2}{5}(\nu_M \nu_X)^3 RT^2 m^5 F_{MX}^J \quad (4)$$

where

$$f^\phi = -A_\phi I^{1/2}/(1 + bI^{1/2}) \quad (5)$$

$$f^\gamma = -A_\phi\left[\frac{I^{1/2}}{1 + bI^{1/2}} + \frac{2}{b}\ln(1 + bI^{1/2})\right] \quad (6)$$

$$B_{MX}^\phi = \beta_{MX}^{(0)} + \beta_{MX}^{(1)}\exp(-x) \quad (7)$$

$$B_{MX}^\gamma = 2\beta_{MX}^{(0)} + 2\beta_{MX}^{(1)}[1 - (1 + x - x^2/2)\exp(-x)]/x^2 \quad (8)$$

$$\alpha = 2.0, \quad b = 1.2, \quad x = \alpha I^{1/2}$$

The parameters, A_ϕ, A_H, and A_J are Pitzer–Debye–Hückel limiting slopes and are discussed elsewhere (44). The temperature dependencies of the parameters $\beta^{(0)}$, $\beta^{(1)}$, C^ϕ, D^ϕ, E^ϕ,

Table V. Mean Activity Coefficients of Aqueous Calcium Chloride Solutions

$m/$(mol kg^{-1})	temp/°C											
	0.0	10.0	20.0	25.0	30.0	40.0	50.0	60.0	70.0	80.0	90.0	100.0
0.001	0.8920	0.8906	0.8889	0.8881	0.8871	0.8851	0.8830	0.8806	0.8781	0.8754	0.8726	0.8695
0.010	0.7352	0.7321	0.7285	0.7266	0.7245	0.7201	0.7153	0.7102	0.7046	0.6987	0.6925	0.6858
0.025	0.6513	0.6474	0.6430	0.6406	0.6380	0.6326	0.6267	0.6203	0.6134	0.6061	0.5983	0.5901
0.050	0.5873	0.5830	0.5780	0.5753	0.5725	0.5663	0.5596	0.5523	0.5445	0.5362	0.5275	0.5182
0.075	0.5524	0.5478	0.5426	0.5397	0.5367	0.5301	0.5230	0.5152	0.5069	0.4981	0.4887	0.4789
0.100	0.5295	0.5248	0.5194	0.5164	0.5133	0.5064	0.4990	0.4909	0.4822	0.4729	0.4632	0.4530
0.200	0.4842	0.4792	0.4733	0.4700	0.4665	0.4590	0.4506	0.4415	0.4318	0.4215	0.4106	0.3993
0.300	0.4670	0.4618	0.4555	0.4520	0.4483	0.4401	0.4310	0.4211	0.4105	0.3993	0.3876	0.3754
0.400	0.4611	0.4557	0.4492	0.4454	0.4414	0.4326	0.4228	0.4121	0.4007	0.3886	0.3760	0.3630
0.500	0.4616	0.4562	0.4493	0.4453	0.4410	0.4315	0.4210	0.4095	0.3972	0.3842	0.3707	0.3568
0.600	0.4665	0.4610	0.4538	0.4495	0.4449	0.4347	0.4234	0.4110	0.3978	0.3839	0.3695	0.3547
0.700	0.4748	0.4693	0.4617	0.4571	0.4522	0.4412	0.4290	0.4156	0.4015	0.3866	0.3713	0.3556
0.800	0.4861	0.4805	0.4724	0.4676	0.4623	0.4505	0.4372	0.4229	0.4076	0.3917	0.3754	0.3587
0.900	0.5000	0.4943	0.4857	0.4806	0.4749	0.4621	0.4478	0.4323	0.4159	0.3989	0.3814	0.3636
1.000	0.5163	0.5105	0.5015	0.4959	0.4897	0.4759	0.4604	0.4437	0.4261	0.4078	0.3892	0.3703
1.200	0.5565	0.5503	0.5399	0.5334	0.5261	0.5098	0.4916	0.4720	0.4515	0.4305	0.4092	0.3878
1.400	0.6069	0.6001	0.5878	0.5801	0.5715	0.5520	0.5305	0.5075	0.4836	0.4593	0.4349	0.4105
1.600	0.6687	0.6607	0.6460	0.6367	0.6263	0.6031	0.5774	0.5503	0.5223	0.4941	0.4659	0.4381
1.800	0.7434	0.7336	0.7157	0.7044	0.6918	0.6638	0.6331	0.6009	0.5680	0.5351	0.5025	0.4706
2.000	0.8331	0.8207	0.7985	0.7846	0.7692	0.7353	0.6985	0.6601	0.6213	0.5827	0.5449	0.5081
2.250	0.9707	0.9531	0.9236	0.9054	0.8856	0.8421	0.7956	0.7477	0.6997	0.6525	0.6067	0.5627
2.500	1.143	1.117	1.077	1.053	1.028	0.9716	0.9125	0.8524	0.7929	0.7350	0.6793	0.6263
2.750	1.357	1.320	1.266	1.234	1.200	1.128	1.053	0.9772	0.9031	0.8317	0.7639	0.6999
3.000	1.624	1.570	1.497	1.454	1.410	1.316	1.220	1.125	1.033	0.9447	0.8618	0.7844
3.250	1.957	1.879	1.778	1.722	1.664	1.542	1.420	1.300	1.184	1.076	0.9745	0.8808
3.500	2.370	2.258	2.121	2.047	1.970	1.813	1.656	1.505	1.361	1.227	1.103	0.9899
3.750	2.880	2.723	2.537	2.438	2.337	2.134	1.935	1.744	1.566	1.401	1.250	1.113
4.000	3.509	3.289	3.039	2.909	2.777	2.514	2.261	2.022	1.801	1.599	1.415	1.250
4.250	4.280	3.977	3.643	3.471	3.299	2.962	2.641	2.343	2.070	1.822	1.600	1.401
4.500	5.221	4.807	4.362	4.137	3.915	3.483	3.080	2.709	2.374	2.073	1.805	1.567
4.750	6.359	5.800	5.213	4.921	4.635	4.087	3.581	3.124	2.714	2.351	2.030	1.748
5.000	7.727	6.979	6.211	5.835	5.469	4.777	4.149	3.588	3.091	2.655	2.274	1.941
5.500	11.29	9.981	8.698	8.088	7.505	6.431	5.484	4.661	3.950	3.338	2.812	2.360
6.000	16.21	13.97	11.89	10.93	10.04	8.434	7.063	5.901	4.921	4.093	3.394	2.804
6.500	22.85	19.04	15.76	14.32	13.01	10.71	8.813	7.244	5.947	4.874	3.984	3.245
7.000	31.81	25.26	20.21	18.12	16.26	13.13	10.62	8.594	6.954	5.622	4.537	3.654
7.500		32.75	25.06	22.11	19.58	15.50	12.34	9.850	7.866	6.280	5.013	4.007
8.000		41.86	30.16	26.10	22.78	17.67	13.87	10.94	8.631	6.812	5.391	4.300
8.500			35.55	30.02	25.76	19.57	15.19	11.86	9.252	7.224	5.677	4.538
9.000			41.62^a	34.05^a	28.63^a	21.30^a	16.37^a	12.68^a	9.796^a	7.567^a	5.916^a	4.774^a
9.500				38.81^a	31.81^a	23.15^a	17.68^a	13.62^a	10.41^a	7.951^a	6.190^a	5.082^a
10.000				45.53^a	36.17^a	25.69^a	19.56^a	15.01^a	11.36^a	8.556^a	6.634^a	5.587^a
10.500						29.97^a	22.82^a	17.50^a	13.08^a	9.681^a	7.469^a	6.510^a
11.000							29.15^a	22.36^a	16.46^a	11.91^a	9.115^a	8.302^a
11.500							42.59^a					

^{a}The validity of the values beyond 9.0 m is questionable.

F^ϕ, and $\bar{C}_{P_2}{}^\circ$ were represented by the equations

$$\beta_{MX}{}^{(0)} = q_1 + q_2(1/T - 1/T_r) + q_3 \ln (T/T_r) + q_4(T - T_r) + q_5(T^2 - T_r^2) \quad (9)$$

$$\beta_{MX}{}^{(1)} = q_6 + q_7(1/T - 1/T_r) + q_9(T - T_r) + q_{10}(T^2 - T_r^2) \quad (10)$$

$$C_{MX}{}^\phi = q_{11} + q_{12}(1/T - 1/T_r) + q_{13} \ln (T/T_r) + q_{14}(T - T_r) + q_{15}(T^2 - T_r^2) \quad (11)$$

$$D_{MX}{}^\phi = q_{16} + q_{17}(1/T - 1/T_r) + q_{18} \ln (T/T_r) + q_{19}(T - T_r) + q_{20}(T^2 - T_r^2) \quad (12)$$

$$E_{MX}{}^\phi = q_{21} + q_{22}(1/T - 1/T_r) + q_{23} \ln (T/T_r) + q_{24}(T - T_r) + q_{25}(T^2 - T_r^2) \quad (13)$$

$$F_{MX}{}^\phi = q_{26} + q_{27}(1/T - 1/T_r) + q_{28} \ln (T/T_r) + q_{29}(T - T_r) + q_{30}(T^2 - T_r^2) \quad (14)$$

$$\bar{C}_{P_2}{}^\circ = q_{31} + q_{32}(T - T_r) + q_{33}(T - T_r)^2 + q_{34}(T - T_r)^3 \quad (15)$$

where $T_r = 298.15$.
   The corresponding equations for $^\phi L$ are

$$B_{MX}{}^L = \partial\beta_{MX}{}^{(0)}/\partial T + (\partial\beta_{MX}{}^{(1)}/\partial T)(2/x^2)[1 - (1 + x)\exp(-x)] \quad (16)$$

$$x = \alpha I^{1/2}$$

$$\partial\beta_{MX}{}^{(0)}/\partial T = -q_2/T^2 + q_3/T + q_4 + 2q_5T \quad (17)$$

$$\partial\beta_{MX}{}^{(1)}/\partial T = -q_7/T^2 + q_9 + 2q_{10}T \quad (18)$$

$$C_{MX}{}^L = \partial C_{MX}{}^\phi/\partial T = -q_{12}/T^2 + q_{13}/T + q_{14} + 2q_{15}T \quad (19)$$

The equations for $D_{MX}{}^L$, $E_{MX}{}^L$ are similar to the equations for $C_{MX}{}^L$ and may be obtained by differentiating eq 12–14.
   The relevant equations for $^\phi C_p$ are

$$B_{MX}{}^J = \frac{\partial^2\beta_{MX}{}^{(0)}}{\partial T^2} + \frac{\partial^2\beta_{MX}{}^{(1)}}{\partial T^2}\left(\frac{2}{x^2}\right)[1 - (1 + x)e^{-x}] + \frac{2}{T}\frac{\partial\beta_{MX}{}^{(0)}}{\partial T} + \frac{2}{T}\frac{\partial\beta_{MX}{}^{(1)}}{\partial T}\left(\frac{2}{x^2}\right)[1 - (1 + x)e^{-x}] \quad (20)$$

$$C_{MX}{}^J = \frac{\partial^2 C_{MX}{}^\phi}{\partial T} + \frac{2}{T}\frac{\partial C_{MX}{}^\phi}{\partial T}$$

$$= q_{13}/T^2 + 2q_{14}/T + 6q_{15} \quad (21)$$

Table VI. Osmotic Coefficients of Aqueous CaCl₂ Solutions

concn/ mol kg⁻¹	temp/°C											
	0	10	20	25	30	40	50	60	70	80	90	100
0.001	0.9634	0.9630	0.9623	0.9620	0.9617	0.9610	0.9602	0.9593	0.9584	0.9574	0.9564	0.9552
0.010	0.9099	0.9087	0.9072	0.9065	0.9056	0.9038	0.9019	0.8997	0.8974	0.8949	0.8922	0.8893
0.025	0.8834	0.8818	0.8800	0.8789	0.8778	0.8755	0.8728	0.8699	0.8668	0.8634	0.8598	0.8558
0.050	0.8670	0.8651	0.8630	0.8618	0.8605	0.8577	0.8545	0.8510	0.8472	0.8430	0.8386	0.8338
0.075	8.8609	0.8589	0.8566	0.8553	0.8539	0.8508	0.8474	0.8435	0.8393	0.8347	0.8297	0.8243
0.100	0.8590	0.8570	0.8545	0.8532	0.8517	0.8484	0.8447	0.8406	0.8360	0.8310	0.8256	0.8199
0.200	0.8660	0.8639	0.8612	0.8597	0.8580	0.8542	0.8498	0.8448	0.8393	0.8332	0.8267	0.8196
0.300	0.8814	0.8793	0.8765	0.8749	0.8730	0.8687	0.8637	0.8581	0.8518	0.8448	0.8373	0.8293
0.400	0.9002	0.8983	0.8954	0.8936	0.8916	0.8869	0.8814	0.8750	0.8680	0.8603	0.8519	0.8430
0.500	0.9213	0.9197	0.9167	0.9148	0.9126	0.9074	0.9013	0.8944	0.8866	0.8782	0.8690	0.8593
0.600	0.9442	0.9429	0.9399	0.9378	0.9354	0.9298	0.9231	0.9155	0.9071	0.8979	0.8880	0.8775
0.700	0.9687	0.9676	0.9646	0.9624	0.9598	0.9537	0.9464	0.9381	0.9290	0.9191	0.9085	0.8972
0.800	0.9947	0.9938	0.9907	0.9883	0.9856	0.9789	0.9710	0.9621	0.9522	0.9416	0.9303	0.9183
0.900	1.022	1.021	1.018	1.016	1.013	1.005	0.9968	0.9871	0.9765	0.9652	0.9531	0.9405
1.000	1.050	1.050	1.046	1.044	1.041	1.033	1.024	1.013	1.002	0.9897	0.9770	0.9636
1.200	1.111	1.111	1.107	1.103	1.100	1.091	1.080	1.068	1.055	1.041	1.020	1.012
1.400	1.176	1.175	1.170	1.167	1.162	1.152	1.139	1.126	1.111	1.096	1.080	1.063
1.600	1.245	1.244	1.238	1.233	1.228	1.216	1.201	1.186	1.169	1.152	1.135	1.117
1.800	1.318	1.316	1.308	1.303	1.297	1.282	1.266	1.248	1.230	1.211	1.191	1.171
2.000	1.394	1.391	1.381	1.375	1.368	1.351	1.333	1.313	1.292	1.271	1.249	1.227
2.250	1.495	1.489	1.477	1.469	1.460	1.441	1.419	1.396	1.372	1.347	1.323	1.298
2.500	1.l600	1.591	1.575	1.566	1.555	1.532	1.507	1.481	1.454	1.426	1.398	1.370
2.750	1.710	1.696	1.677	1.666	1.653	1.627	1.598	1.568	1.537	1.505	1.474	1.443
3.000	1.823	1.805	1.781	1.768	1.753	1.722	1.690	1.655	1.620	1.585	1.550	1.515
3.250	1.939	1.915	1.887	1.871	1.854	1.819	1.782	1.744	1.705	1.665	1.626	1.587
3.500	2.056	2.027	1.993	1.975	1.956	1.916	1.875	1.832	1.788	1.745	1.701	1.658
3.750	2.175	2.140	2.100	2.079	2.058	2.013	1.967	1.919	1.871	1.823	1.775	1.727
4.000	2.293	2.252	2.207	2.183	2.159	2.109	2.057	2.005	1.952	1.899	1.847	1.794
4.250	2.409	2.362	2.311	2.285	2.258	2.202	2.146	2.089	2.031	1.974	1.916	1.858
4.500	2.524	2.471	2.414	2.384	2.354	2.293	2.232	2.169	2.107	2.045	1.982	1.919
4.750	2.636	2.576	2.513	2.480	2.447	2.381	2.314	2.246	2.179	2.112	2.045	1.977
5.000	2.744	2.678	2.608	2.572	2.536	2.464	2.391	2.319	2.247	2.175	2.103	2.030
5.500	2.947	2.867	2.783	2.741	2.699	2.614	2.531	2.449	2.368	2.287	2.205	2.123
6.000	3.132	3.033	2.934	2.884	2.836	2.740	2.646	2.554	2.464	2.375	2.285	2.194
6.500	3.298	3.174	3.056	2.999	2.943	2.835	2.732	2.631	2.533	2.437	2.340	2.243
7.000	3.453	3.291	3.149	3.083	3.020	2.900	2.787	2.679	2.575	2.472	2.370	2.268
7.500		3.390	3.213	3.136	3.064	2.934	2.813	2.699	2.588	2.480	2.375	2.273
8.000		3.478	3.254	3.163	3.082	2.940	2.813	2.695	2.579	2.466	2.359	2.261
8.500			3.281	3.171	3.078	2.925	2.794	2.672	2.553	2.437	2.329	2.240
9.000			3.308	3.174	3.066	2.900	2.768	2.645	2.523	2.402	2.295	2.220

The equations for $D_{MX}{}^{J}$, $E_{MX}{}^{J}$, and $F_{MX}{}^{J}$ are similar to the equations for $C_{MX}{}^{J}$.

The differential heats of dilution (39) of aqueous CaCl₂ solutions were converted into relative partial molal enthalpies of solvent ($\bar{L}_1$) and then fitted to the equation

$$\bar{L}_1 = -\frac{m^2}{55.5087} \frac{\partial^{\phi}L}{\partial m} \qquad (22)$$

where $\partial^{\phi}L/\partial m$ was obtained by differentiating eq 3 with respect to molality (m).

The osmotic coefficients, activity coefficients, apparent molal enthalpies, apparent molal heat capacities, and differential heats of dilution data were fitted to eq 1–4 and 22 in a single nonlinear least-squares procedure using an IBM-3081 computer. The apparent molal enthalpy and differential heats of dilution were given a weight of $1/(\nu RT^2)$ and apparent molal heat capacities were weighted as $1/(\nu RT)$. None of the known concentration-based weighting procedures improved the quality of the fit and hence, were not adopted. Initially the coefficients q_1, q_6, q_{11}, q_{16}, q_{21}, and q_{26} were evaluated by using the 25 °C data of Rard, Habenschuss, and Spedding (3). These coefficients were essentially identical with the values communicated by Rogers (5).

Next, the coefficients q_{31}, q_{32}, q_{33}, and q_{34} were evaluated by using the apparent molal heat capacities at zero concentration ($\bar{C}_{p_2}{}^{\circ}$) values listed in Table III. These $\bar{C}_{p_2}{}^{\circ}$ values were obtained by fitting the apparent molal heat capacity data

at each temperature with the following form of the Pitzer equation (40–43):

$$^{\phi}C_{p_2} = \bar{C}_{p_2}{}^{\circ} + \nu|Z_M Z_X|A_J[1/2b]\ln(1 + bI^{1/2}) -$$
$$2(\nu_M\nu_X)RT^2 mB - (\nu_M\nu_X)^{3/2}RT^2 m^2 C \quad (23)$$

where

$$B = \beta_J{}^{(0)} + \beta_J{}^{(1)}(2/x^2)\{1 - (1 + x)\exp(-x)\} \quad (24)$$

and $x = 2I^{1/2}$. Then these $\bar{C}_{p_2}{}^{\circ}$ values were fitted to eq 15 and the resulting coefficients (q_{31}–q_{34}) are listed in Table IV.

Finally, the remaining q's were evaluated by using a total of 421 data points (39 activity coefficients, 153 osmotic coefficients, 72 apparent molal enthalpies, 110 apparent molal heat capacities, and 47 differential heats of dilution). All the data were given a weight of either 1 or 0. Only data points with a deviation of three σ or more were given zero weight. On the basis of this criterion 66 points were given zero weights; 45 of these deleted points are shown in Tables I and II. Of the remaining 21 deleted data points, 15 belong to the differential heats of dilution (39). A listing of the data points that were deleted and are not included in Tables I and II is available as supplementary material (see paragraph at end of text regarding supplementary material). The final values of q's were calculated by using the 355 data points in the least-squares analysis. These q's are listed in Table IV.

The q's listed in Table IV fitted all the activity coefficients with a standard deviation of 0.0031 and all the osmotic coef-

Table VII. Apparent Molal Enthalpy (kJ mol⁻¹) of Aqueous Calcium Chloride Solutions

| concn/ (mol kg⁻¹)	temp/°C											
	0	10	20	25	30	40	50	60	70	80	90	100
0.001	0.1931	0.2352	0.2819	0.3070	0.3332	0.3894	0.4507	0.5175	0.5904	0.6699	0.7568	0.8517
0.01	0.5332	0.6531	0.7871	0.8592	0.9347	1.096	1.273	1.465	1.674	1.902	2.150	2.420
0.025	0.7600	0.9347	1.131	1.237	1.348	1.587	1.847	2.130	2.438	2.773	3.136	3.531
0.05	0.9669	1.194	1.452	1.591	1.738	2.052	2.396	2.769	3.175	3.615	4.092	4.609
0.075	1.100	1.362	1.661	1.824	1.995	2.363	2.765	3.202	3.676	4.189	4.743	5.343
0.10	1.198	1.488	1.820	2.000	2.191	2.601	3.049	3.536	4.064	4.635	5.251	5.916
0.20		1.807	2.233	2.466	2.712	3.242	3.822	4.453	5.134	5.867	6.654	7.499
0.30		2.002	2.498	2.770	3.004	3.674	4.350	5.082	5.871	6.717	7.623	8.592
0.40		2.141	2.699	3.004	3.326	4.018	4.772	5.586	6.462	7.399	8.399	9.466
0.50		2.246	2.864	3.201	3.554	4.312	5.134	6.020	6.969	7.982	9.062	10.21
0.60		2.330	3.007	3.373	3.757	4.575	5.459	6.408	7.422	8.502	9.651	10.87
0.70		2.397	3.134	3.530	3.942	4.818	5.760	6.766	7.837	8.976	10.19	11.47
0.80		2.454	3.251	3.675	4.116	5.047	6.042	7.101	8.225	9.417	10.68	12.02
0.90		2.502	3.360	3.813	4.282	5.267	6.312	7.420	8.592	9.833	11.15	12.54
1.00		2.545	3.465	3.947	4.443	5.479	6.573	7.726	8.943	10.23	11.59	13.03
1.20		2.623	3.666	4.205	4.756	5.892	7.077	8.315	9.612	10.98	12.41	13.94
1.40		2.699	3.867	4.463	5.066	6.298	7.568	8.883	10.25	11.68	13.19	14.79
1.60		2.784	4.076	4.726	5.381	6.706	8.056	9.443	10.88	12.37	13.93	15.59
1.80		2.885	4.297	5.001	5.706	7.120	8.548	10.00	11.49	13.04	14.66	16.37
2.00	1.455	3.006	4.535	5.292	6.045	7.545	9.048	10.57	12.11	13.71	15.38	17.13
2.25	1.482	3.194	4.862	5.682	6.493	8.097	9.688	11.28	12.90	14.56	16.27	18.08
2.50	1.566	3.427	5.226	6.104	6.971	8.674	10.35	12.02	13.70	15.41	17.18	19.03
2.75	1.710	3.708	5.629	6.563	7.482	9.279	11.04	12.78	14.52	16.29	18.10	20.00
3.00	1.916	4.038	6.073	7.059	8.027	9.915	11.75	13.57	15.37	17.19	19.05	20.99
3.25	2.181	4.419	6.558	7.593	8.608	10.58	12.50	14.38	16.24	18.20	20.03	22.00
3.50	2.504	4.848	7.085	8.166	9.224	11.28	13.27	15.22	17.15	19.08	21.04	23.06
3.75	2.880	5.322	7.652	8.776	9.876	12.01	14.07	16.09	18.08	20.06	22.08	24.14
4.00	3.306	5.842	8.258	9.423	10.56	12.77	14.91	16.98	19.03	21.08	23.15	25.27
4.50	4.284	7.000	9.580	10.82	12.03	14.38	16.65	18.85	21.02	23.19	25.38	27.63
5.00	5.407	8.301	11.04	12.35	13.63	16.11	18.49	20.81	23.10	25.39	27.72	30.12
5.50	6.664	9.736	12.62	14.00	15.34	17.93	20.41	22.84	25.24	27.65	30.13	32.72
6.00	8.079	11.31	14.32	15.76	17.15	19.83	22.40	24.91	27.42	29.96	32.59	35.37
6.50		13.06	16.16	17.62	19.05	21.79	24.43	27.02	29.61	32.27	35.05	38.02
7.00		15.06	18.14	19.61	21.03	23.79	26.47	29.12	31.80	34.56	37.47	40.59
7.50			20.32	21.72	23.10	25.82	28.51	31.21	33.96	36.81	39.80	43.00
8.00			22.75	24.00	25.27	27.85	30.51	33.25	36.08	38.99	42.01	45.14
8.50				26.49	27.53	29.86	32.46	35.24	38.15	41.11	44.05	46.92
9.00				29.27	29.94	31.84	34.31	37.16	40.17	43.15	45.89	48.20
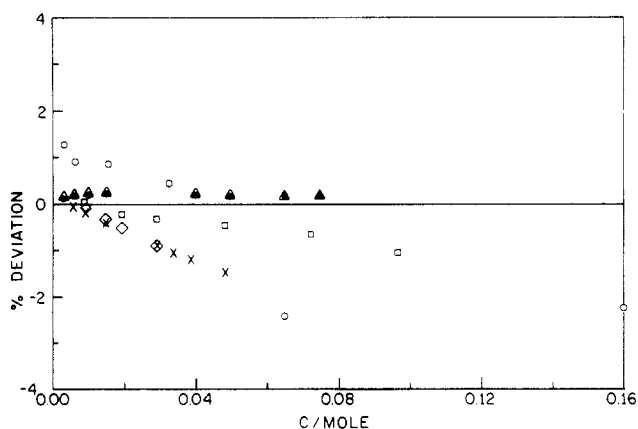
Figure 1. Percentage deviations of the experimental activity and osmotic coefficients at low concentrations from the corresponding values calculated by using the present fit: (●) McLeod and Gordon (6), 15 °C; (△) McLeod and Gordon (6) 35 °C; (□) Mussini and Pagella (7), 40 °C; (X) Mussini and Pagella (7), 55 °C; (◇) Mussini and Pagella (7), 70 °C; (O) Plake (14) boiling point elevation.
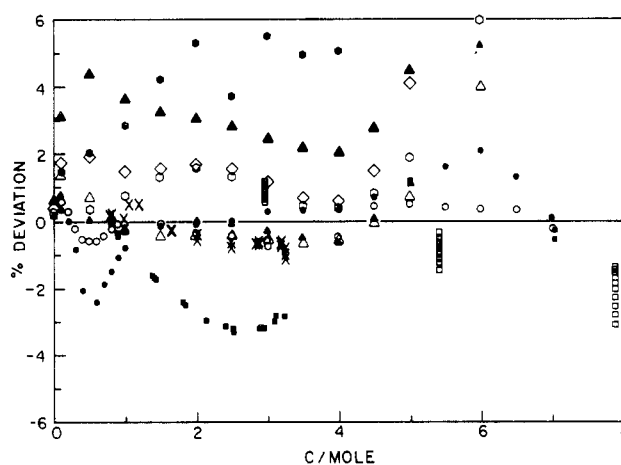

Figure 2. Percentage deviations of the experimental activity and osmotic coefficients from the corresponding values calculated by using the present fit: (●) Platford (9), φ at 0 °C; (O) Childs and Platford (10), φ at 15 °C; (X) Holmes, Baes, and Mesmer (16), φ at 382 K; (■) Holmes, Baes, and Mesmer (16), φ at 413.8 K; (□) Jakli and Van Hook (8), φ at 20–90 °C; (●) Phutela and Pitzer (4) fit, γ at 0 °C; (◇) Phutela and Pitzer (4) fit, γ at 50 °C; (▲, large size) Phutela and Pitzer (4) fit, γ at 100 °C; (O) Phutela and Pitzer (4) fit, φ at 0 °C; (▲, small size) Phutela and Pitzer fit, φ at 50 °C; (△) Phutela and Pitzer fit, φ at 100 °C.

ficients, except the Holmes, Baes, and Mesmer (16) data at 413.8 K, with a standard deviation of 0.023. Alternatively, the activity coefficient data could be reproduced with an average deviation of ±0.39% and osmotic coefficient data within ±0.96%. In other words, these *q*'s can reproduce the activity and osmotic coefficients of aqueous $CaCl_2$ solutions with an average precision of ±1.0% from 0 to 100 °C up to a concentration of 9.0 m or to the limit of solubility whichever is

lower. Figures 1 and 2 show the percentage deviation of the activity and osmotic coefficient data from the values calculated in the present work. The deviations of the osmotic coefficients predicted by Phutela and Pitzer's (4) fit are also shown in these

Table VIII. Apparent Molal Heat Capacity (J K^{-1} mol^{-1}) of Aqueous Calcium Chloride Solutions

| concn/ (mol kg^{-1})	temp/°C											
	0	10	20	25	30	40	50	60	70	80	90	100
0.00	−377.8	−328.4	−290.6	−275.7	−263.3	−245.4	−236.0	−234.2	−238.8	−249.0	−263.7	−281.9
0.001	−373.8	−324.0	−285.7	−270.6	−257.9	−239.5	−229.6	−227.2	−231.2	−240.7	−254.6	−272.0
0.01	−366.5	−315.7	−276.5	−260.9	−247.8	−228.5	−217.6	−214.1	−217.0	−225.2	−237.8	−253.7
0.025	−361.4	−309.9	−269.9	−254.0	−240.5	−220.5	−208.9	−204.6	−206.7	−214.1	−225.8	−240.7
0.05	−356.7	−304.2	−263.4	−247.1	−233.2	−212.5	−200.2	−195.2	−196.6	−203.2	−214.1	−228.1
0.075	−353.5	−300.3	−258.9	−242.3	−228.2	−206.9	−194.1	−188.6	−189.5	−195.6	−206.0	−219.5
0.10	−351.1	−297.3	−255.4	−238.5	−224.2	−202.5	−189.3	−183.4	−183.9	−189.7	−199.7	−212.8
0.20	−344.3	−288.m	−245.3	−227.8	−212.8	−189.9	−175.5	−168.6	−168.2	−173.0	−182.1	−194.4
0.30	−339.0	−282.2	−237.8	−219.8	−204.4	−180.7	−165.6	−158.1	−157.1	−161.4	−170.0	−181.7
0.40	−333.8	−276.3	−231.3	−213.0	−197.3	−173.1	−157.6	−149.7	−148.2	−152.2	−160.4	−171.7
0.50	−328.4	−270.5	−225.1	−206.7	−190.8	−166.4	−150.6	−142.4	−140.7	−144.4	−152.3	−163.3
0.60	−322.6	−264.6	−219.2	−200.7	−184.8	−160.2	−144.4	−136.0	−134.2	−137.6	−145.3	−155.9
0.70	−316.5	−258.6	−213.3	−194.8	−179.0	−154.5	−138.7	−130.3	−128.3	−131.6	−139.0	−149.4
0.80	−310.0	−252.4	−207.4	−189.1	−173.4	−149.1	−133.4	−125.0	−123.0	−126.2	−133.4	−143.5
0.90	−303.2	−246.1	−201.5	−183.4	−167.9	−143.9	−128.4	−120.2	−118.2	−121.4	−128.4	−138.2
1.00	−296.1	−239.1	−195.7	−177.8	−162.5	−138.9	−123.7	−115.7	−113.8	−116.9	−123.8	−133.3
1.20	−281.4	−226.5	−183.9	−166.7	−152.0	−129.4	−115.0	−107.5	−105.9	−109.0	−115.7	−124.7
1.40	−266.3	−213.2	−172.3	−155.8	−141.8	−120.4	−106.9	−100.1	−98.98	−102.3	−108.8	−117.5
1.60	−251.1	−200.0	−160.8	−145.2	−131.9	−111.8	−99.32	−93.37	−92.76	−96.34	−102.9	−111.3
1.80	−236.1	−187.0	−149.6	−134.8	−122.2	−103.5	−92.14	−87.06	−87.07	−91.03	−97.74	−106.0
2.00	−221.6	−174.4	−138.8	−124.7	−112.9	−95.49	−85.27	−81.08	−81.78	−86.20	−93.13	−101.4
2.25	−204.5	−159.5	−125.8	−112.7	−101.7	−85.88	−77.01	−73.95	−75.55	−80.62	−87.98	−96.37
2.50	−188.7	−145.5	−113.6	−101.3	−91.10	−76.67	−69.05	−67.08	−69.58	−75.38	−83.28	−92.00
2.75	−174.2	−132.6	−102.1	−90.48	−81.00	−67.82	−61.34	−60.37	−63.76	−70.31	−78.82	−88.01
3.00	−161.0	−120.6	−91.39	−80.34	−71.42	−59.32	−53.83	−53.78	−57.99	−65.28	−74.42	−84.15
3.25	−149.0	−109.6	−81.38	−70.81	−62.36	−51.15	−46.52	−47.27	−52.22	−60.18	−69.93	−80.20
3.50	−138.1	−99.47	−72.01	−61.84	−53.77	−43.32	−39.39	−40.81	−46.39	−54.94	−65.21	−75.95
3.75	−127.8	−89.95	−63.19	−53.35	−45.62	−35.80	−32.46	−34.43	−40.51	−49.49	−60.16	−71.22
4.00	−118.1	−80.93	−54.83	−45.30	−37.86	−28.59	−25.74	−28.13	−34.55	−43.81	−54.68	−65.86
4.25	−108.7	−72.25	−46.84	−37.62	−30.47	−21.70	−19.25	−21.93	−28.54	−37.88	−48.71	−59.74
4.50	−99.28	−63.77	−39.14	−30.26	−23.41	−15.12	−13.01	−15.86	−22.50	−31.70	−42.22	−52.77
4.75	−89.81	−55.41	−31.69	−23.19	−16.67	−8.88	−7.05	−9.97	−16.45	−25.27	−35.19	−44.91
5.00	−80.17	−47.11	−24.46	−16.40	−10.25	−2.98	−1.40	−4.28	−10.43	−18.64	−27.66	−36.17
5.50	−60.69	−30.92	−10.87	−3.83	1.49	7.64	8.85	6.35	1.34	−4.97	−11.31	−16.37
6.00	−42.87	−16.67	0.67	6.69	11.19	16.37	17.51	15.82	12.51	8.80	5.97	5.31
6.50				13.45	17.62	22.66	24.39	24.04	22.81	21.93	22.67	26.35
7.00				13.63	18.72	25.68	29.41	31.14	32.09	33.49	36.61	42.78
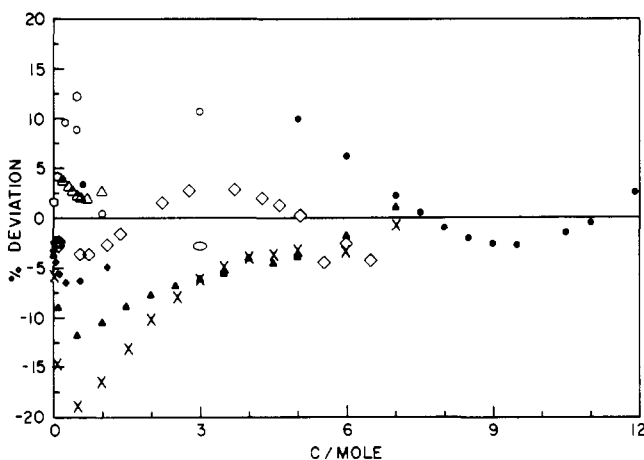
Figure 3. Percentage deviations of the experimental relative apparent molal enthalpy values from the values calculated by using the present fit: (◊) Parker, Garvin, and Staples (*18*), 25 °C; (△) Leung and Millero (*20*), 30 °C; (●) Lilich, Chernykh, and Rumyantseva (*22*), 50 °C; (○) Lilich, Chernykh, and Rumyantseva (*22*), 0 °C; (○) Perachon and Thourey (*21*), 25 °C; (♦) Richard and Dole (*23*), 20 °C; (○) Phutela and Pitzer fit (*4*), 10 °C; (▲) Phutela and Pitzer fit (*4*), 50 °C; (X) Phutela and Pitzer fit, 100 °C.

figures. From Figures 1 and 2 it is evident that the experimental activity and osmotic coefficients are scattered around our calculated line but more on the negative side whereas most of the values calculated by the Phutela and Pitzer (*4*) parameters deviate positively.

The present fit reproduces all of the apparent molal enthalpy (*$^\phi L$*) data with an average deviation of ±3.5%. The deivations of *$^\phi L$* data and the values calculated by using the Phutela and

Pitzer (*4*) fit from the values calculated by using the present fit are shown in Figure 3. Figure 3 shows that the *$^\phi L$* data are scattered on both sides of the present fit whereas the values calculated by using the Phutela and Pitzer (*4*) fit are mostly on the negative side. However, the *$^\phi L$* values at 0 °C calculated by using the present fit show some sinusoidal nature in the concentration range 0.1–2.0 *m*. Therefore, these values are not listed in Table VII. But, these values can be approximately interpolated from a plot of the values listed under 0 °C against the square root of molality. Also, the present fit reproduces all the specific heat data considered with an average deviation of ±4.61%. This compares well with the average experimental error of ±5% in the specific heat data. The deviations of the experimental apparent molal heat capacities (*$^\phi C_{p_2}$*) from the values calculated by using the present fit are shown in Figure 4. Figure 4 shows that about 65% of the data are within the ±5% deviation range and the higher deviations beyond the concentration of 3 *m* are due to the fact that a difference of 1 cal or 4.184 J in a value of 50 J reflects about 8% deviation. The Harrison and Perman (*39*) data on the differential heats of dilution appear to have a much higher experimental error than the recent apparent molal enthalpy and heat capacity data. Their data could only be fitted with a deviation of ±9.7%. Therefore, the Harrison and Perman (*39*) data were given a weight of 0.25 in the overall fit. It should be noted that the temperature derivatives of the activity and osmotic coefficient expressions are in agreement with the experimental calorimetric data available over the temperature range considered.

The calculated values of the activity coefficients, osmotic coefficients, relative apparent molal enthalpies, and apparent molal heat capacities at 12 different temperatures and rounded molalities are given in Tables V–VIII, respectively.
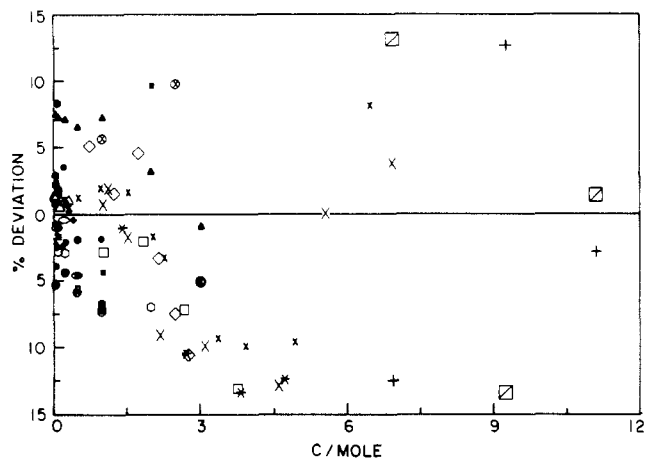
Figure 4. Percentage deviations of the experimental apparent molal heat capacity values from the values calculated by using the present fit: (X, small and thick) Perron, Roux, and Desnoyers (28), 25 °C; (△) Perron, Desnoyers, and Millero (26), 25 °C; (♦) Spitzer, Singh, McCurdy, and Hepler (29), 25 °C; (□) Vasilev, Fedyainov, and Kurenkov (30), 25 °C; (*) Fedyainov, Vasilev, and Karapet'yants (31), 25 °C; (◊) Karapet'yants, Vasilev, and Fedyainov (32), 25 °C; (X, large and thin) Rutskov (33), 25 °C; (▲) Gates, White, and Wood (34), 306.21 K; (○) Gates, White, and Wood (34), 324.39 K; (□) Gates, White, and Wood (34), 350.06 K; (⊕) Gates, White, and Wood (34), 349.86 K; (⊗) Gates, White, and Wood (34), 403.95 K; (●) Gates, White, and Wood (34), 451.18 K; (+) Rutskov (33), 50 °C; (▨) Rutskov (33), 75 °C; (●) Saluja (36), 75 °C; (○) Saluja (36), 100 °C.

From this review of the available experimental data it is evident that there is a need for experimental measurements in the temperature range 0–25 °C. Activity coefficient data beyond 0.1 m are lacking over the entire temperature range of 0–100 °C. The $\bar{C}_{p_2}^{\circ}$ curve appears to take a sharp drop below 25 °C and there are very few experimental data available to definitely confirm this. Also, $^{\phi}L$ data beyond 50 °C are lacking.

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Registry No. $CaCl_2$, 10043-52-4.

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