Thermodynamics of Calcium Chloride in Concentrated Aqueous Solutions and in Crystals

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A variety of experimental measurements for $CaCl_2$(aq) in the range from 5 mol·kg^{-1} to saturation at temperatures from 323 to 523 K, including the vapor pressures of the saturated solutions, are combined to yield a comprehensive thermodynamic treatment. The new equation was generated first for the osmotic coefficient ϕ. It was fitted to the value of ϕ and its molality derivative at 5 mol·kg^{-1} to a new comprehensive treatment for dilute solutions of Holmes et al. (*J. Chem. Thermodyn.* **1994**, *26*, 271), and to the available data for higher molality. The combination of the equation of Holmes et al. to 5 *m* and the new equation to saturation molality then yields a complete treatment for aqueous $CaCl_2$. The chemical potentials in the saturated solution were then used, with other information, to give a general treatment of the thermodynamics of solid $CaCl_2$ and its hydrates with 1/3, 1, and 2 H_2O. This treatment for the range above 323 K supplements a recent treatment of Pitzer and Shi (*J. Solution Chem.* **1993**, *22*, 99) for lower temperatures which considered both aqueous $CaCl_2$, and its solid hydrates with 4 and 6 H_2O.

Introduction

The thermodynamic properties of aqueous $CaCl_2$ have been accurately measured over a wide temperature range to about 5 mol·kg^{-1}. Much less is known, however, about the more concentrated solutions ranging to saturation molalities m_s as high as 30.8 mol·kg^{-1} at 523 K. For the range of moderate concentrations, Holmes, Busey, Simonson, and Mesmer (*1*) (HBSM) have very recently presented a comprehensive equation of state which gives an accurate representation of various properties to 523 K and 4.75 mol·kg^{-1}. In this paper we present an equation extending these properties to saturation molality as accurately as present experimental information allows. At saturation molality there is equilibrium with the saturating solid which varies from the hexahydrate at 298 K and several intermediate hydrates to anhydrous $CaCl_2$ above 503 K. The relationship between solution and solid properties is important in the selection of reliable data, and results, eventually, in new or improved values for certain solid properties.

Recently, Pitzer and Shi (*2*) presented a treatment for $CaCl_2$ in concentrated solution and hydrated crystals for the more limited temperature range to 373 K. The very recent HBSM equation was not available for that project, which was based for the moderate molality range on the values of the CODATA study of Garvin et al. (*3*) and those of Ananthaswamy and Atkinson (*4*) (AA). While these two treatments agree very closely at and near 298 K, their uncertainties increase rapidly with temperature. There is no need to revise the values of Pitzer and Shi (*2*) for the range 298–318 K for both the solution and the hexa- and tetrahydrate solids; these values are accepted and listed in the summary of this paper. In the 323–373 K range, the present treatment has the advantage of some improvements, but the final results differ only slightly for the solution and the dihydrate solid properties remain unchanged. The primary advance of this research is for the range above 373 K.

While it would be desirable to add terms to a "moderate-molality" equation to obtain representation of properties at higher molality, this is very cumbersome, as the CODATA and AA studies show, even for the more limited range to 373 K and 13.6 mol·kg^{-1}. Such a procedure is even less practical for our present range to 523 K and 30.8 mol·kg^{-1}. Several researchers have noted the sudden change in properties of $CaCl_2$(aq) near 6 or 7 mol·kg^{-1} in the 298–373 K range (*2*, *5*, *6*). Phutela and Pitzer (*5*) discussed this change in terms of a shift from a dominantly H_2O inner shell around Ca^{2+} below 5 mol·kg^{-1} to a mixed Cl^- and H_2O shell at higher molality. Thus, we do not attempt a single equation for the full range of molality; rather, we adopt a rather simple equation for the range 4.75 mol·kg^{-1} to the saturation molality m_s. By requiring agreement at 4.75 and 5.0 mol·kg^{-1} with the HBSM equation, both the value and the first derivative agree in this range. There are rather extensive measurements of the vapor pressure over saturated solutions in equilibrium with solids, and these yield values of the osmotic coefficient ϕ at m_s. At intermediate molalities there is a very important set of vapor pressure measurements at 523 K of Ketsko, Urusova, and Valyashko (*7*) (KUV), which determine the full curve at that temperature. The full curve is also determined less simply but with reasonable accuracy in the 323–363 K range. The similarity of properties at 363 and 523 K allows a very plausible but not rigorous determination of a single equation for the entire range including the intermediate temperatures between 363 and 523 K. This equation, determined first for the osmotic coefficient, also yields the activity coefficient when combined with the HBSM equation at $m = 5.0$ mol·kg^{-1}. And with both osmotic and activity coefficients known at the saturation molality, the Gibbs energy difference of the solid from that of $CaCl_2$(aq) in the standard state is determined. At 523 K there is independent information for comparison, and agreement is found within the uncertainties.

Equation for Aqueous $CaCl_2$. Treatments for 363.15 and 523.15 K. The equations for these two temperatures are the primary basis for the general equation which is an interpolation guided by the limited experimental information available at the intermediate temperatures. At 523.15 K, there is a full array of measured vapor pressures from KUV (*7*) for the range 5 mol·kg^{-1} to saturation at 30.85 mol·kg^{-1}. These were converted to fugacities with the equation of Hill (*8*) for pure steam. Also, small adjustments were made to place all data at the saturation pressure of pure H_2O, 39.7 bar. Then the osmotic coefficient was calculated for each composition, with the results shown as circles in Figure 1 where the curve for the HBSM equation appears as a thin solid line marked at each end. It is apparent that an extrapolation of the HBSM equation from 4.75 to 5.0 mol·kg^{-1}

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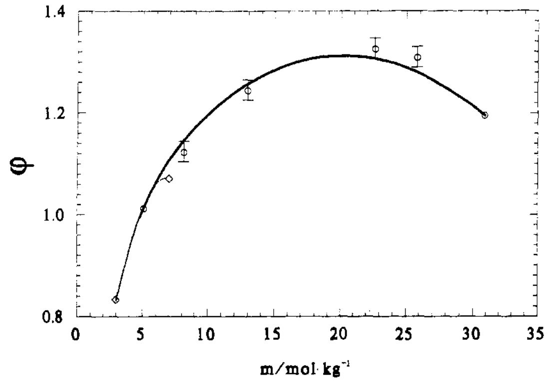

Figure 1. Osmotic coefficient of $CaCl_2(aq)$ at 523.15 K: ◇, HBSM (*1*); ○, Ketsko et al. (*7*). Circles are measurements of Ketsko et al. (*7*), while the heavy curve is from this research. The thin line with diamonds at each end is the curve from HBSM (*1*); the dashed extrapolation only shows significant departure above 6.5 mol·kg^{-1}.

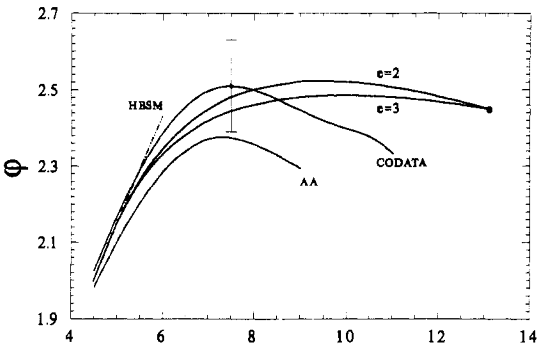

Figure 2. Osmotic coefficient at 363.15 K with curves from the equations or tables of AA (*4*), CODATA (*3*), and HBSM (*1*). The last curve is a dotted-dashed line in its extrapolation above 5 *m*. The curves $e = 2$ and $e = 3$ are from this research with the indicated value of *e* in eq 1 (see text for further details).

is valid. Indeed, the extrapolated HBSM equation is well within the uncertainty of the KUV data to at least 6.5 mol·kg^{-1} at 523 K, which is far beyond its stated range of validity.

It is evident from Figure 1 that the experimental results of KUV agree at $m = 5$ mol·kg^{-1} almost exactly with the HBSM equation. A simple quadratic equation represents the data from 4.75 to 30.8 mol·kg^{-1} satisfactorily, while the slope at 4.75 mol·kg^{-1} can be adjusted to that of the HBSM equation with a small term involving a negative power of *m*. Thus, the equation adopted for the osmotic coefficient is

$$\phi = a + bm + cm^2 + dm^{-e} \tag{1}$$

With the wide range in *m* from 4.75 to 30.8 mol·kg^{-1}, the term in m^2 is significant, even with a very small coefficient *c* near -0.001 kg^2·mol^{-2}. The final term, however, is very small and is insensitive to the exact exponent $-e$. In contrast, we will find that at 363.15 K the final term is significant and sensitive to the choice of exponent while, with the much smaller range in *m*, the term cm^2 has little effect for any value of *c* near -0.001 kg^2·mol^{-2}. Thus, both *c* and *e* will be assumed to be constants independent of temperature, with *c* determined essentially from data at 523.15 K and *e* from data at 363.15 K.

At temperatures from 298.15 to 363.15 K, there are, in addition to the HBSM equation valid to at least 4.75 mol·kg^{-1}, the two relatively comprehensive treatments of CODATA (*3*) and AA (*4*) which extend, with gradually decreasing accuracy to 11 and 9 mol·kg^{-1}, respectively. Both treatments include some less certain information for 373.15 K, but it seems best to focus on 363.15 K for the present project. Figure 2 shows for 363.15 K the HBSM, CODATA, and AA curves over the range from 4.5 mol·kg^{-1} to saturation at $m = 13.1$ mol·kg^{-1}. The experimental osmotic coefficient at saturation was reported by Collins and Menzies (*9*); an older value of Roozeboom (*10*) agrees within its lower precision. One first notes that none of the published equations (*1, 3, 4*) have trends at high *m* consistent with the known φ at saturation molality. In the range 4.5–5.0 mol·kg^{-1}, the HBSM, CODATA, and AA equations all agree rather closely, with the HBSM curve intermediate and very close to that of CODATA. Thus, extrapolation of the HBSM equation to $m = 5.0$ mol·kg^{-1} is valid at this temperature as well as at 523 K. But at higher molality, the HBSM curve clearly deviates. At $m = 7.5$ mol·kg^{-1}, the stated uncertainty of the CODATA equation, as shown in Figure 2, extends close to the AA curve and suggests that the true curve lies between the AA and CODATA curves in this molality range. Alternate curves for eq 1 with $c = -0.001$ kg^2·mol^{-2}; *a*, *b*, and *d* determined to fit the HBSM curve at $m/(\text{mol·kg}^{-1}) = 4.75, 5.0$, and the experimental value at 13.1 (saturation); and *e* either 2 or 3 are shown. Each yields an acceptable curve. Since the CODATA study is more recent than the AA report and includes some additional information, we favored the curve closer to that of CODATA in the 5–8 mol·kg^{-1} range. Thus, the value $e = 2$ was adopted. At this time the uncertainty, however, is at least that of the difference between the $e = 2$ and $e = 3$ curves.

With the adoption of $e = 2$ for all temperatures, eq 1 was fitted to the data at 523.15 K with primary emphasis on the HBSM values at $m/(\text{mol·kg}^{-1}) = 4.75$ and 5.0 and the experimental value at saturation molality. This yields $c = -0.0010$ kg^2·mol^{-2} and the curve in Figure 1. While the points near 23 and 26 mol·kg^{-1} suggest a slightly higher curve, these are only single measurements with uncertainties which we estimated to extend to the curve shown. For saturation molality, there are several measurements, whose average value is shown, and this was given dominant weight.

Before further calculations, it is desirable to examine the maximum molality for which the HBSM equation is valid to the accuracy of importance in this study, ±0.01 in φ. From Figure 1, this range is to $m = 5.5$ mol·kg^{-1} at 523 K, whereas we noted above the validity to $m = 5.0$ mol·kg^{-1} at 363 K. At lower temperatures deviation is detectable at slightly lower molalities, but a comparison with CODATA at 323 K shows accurate agreement at $m = 4.75$ mol·kg^{-1} and a deviation of only 0.02 in φ at $m = 5.0$ mol·kg^{-1}. Since it is an advantage to use as high a molality as possible in fitting the new equation to the HBSM pattern, we assumed validity to 5.0 *m* throughout and fitted at $m/(\text{mol·kg}^{-1}) = 4.75$ and 5.0 to obtain agreement also in the derivative of φ.

Treatment for Other Temperatures. At other temperatures from 323 to 473 K, there are measured values of the water activity of the saturated solution. The more accurate values of Collins and Menzies (*9*) extend to 398 K, while those of Roozeboom (*10*) extend over the entire range to 473 K. The 1928 International Critical Tables (*11*) give recommended values up to 449 K which are close to those of Roozeboom, but not identical. The other information considered by ICT and the basis of selection are not clear, but the difference is not large. Corrections of pressures to fugacities were made at the higher temperatures where they are significant, and values were calculated for the activity of water.

For the calculation of the osmotic coefficient, the differences in values reported for m_s, the molality at saturation, represent larger uncertainties than those of the activity. CODATA (*3*) made well-justified recommendations for m_s which we accepted for all temperatures below 449 K. At 449 K there are

Table 1. Properties of Concentrated $CaCl_2(aq)$ from 323 to 449 K Including ΔG° of Reaction from $CaCl_2 \cdot 2H_2O(s)$ and S°_{298} for the Solid

			ϕ_{sat}		$\ln \gamma_\pm$ at			
T/K	P/bar	$m_{sat}/(mol \cdot kg^{-1})$	exptl	eq	5 mol·kg^{-1}	m_{sat}	$-\Delta_{soln}G^\circ/RT$	$S^\circ_{298}(s)/R$
323.15	1	11.6_5	2.84_5	2.85_5	1.491_2	3.41_3	15.40	24.87
333.15	1	11.9_5	2.75	2.75_3	1.349_5	3.21_2	14.91	24.77
343.15	1	12.2_0	2.67	2.65_5	1.201_2	2.99_8	14.38	24.71
353.15	1	12.6_5	2.55	2.55_0	1.045_9	2.78_8	13.87	24.65
363.15	1	13.1_0	2.45	2.44_8	0.885_4	2.56_5	13.33	24.61
373.15	1	13.6_0	2.35	2.34_6	0.718_7	2.33_6	12.77	24.60
383.15	1.4	14.2_5	2.23	2.24_2	0.546_9	2.10_3	12.21	24.60
398.15	2.3	15.4	2.07_5	2.08_8	0.279_8	1.74_0	11.34	24.63
413.15	3.6	16.7	1.92	1.94_0	0.002_0	1.35_7	10.40	24.73
433.15	6.2	19.5	1.73	1.73_8	-0.385_4	0.83_2	9.13	24.87
449	9.1	26.7_5[a]	1.41	1.45_3	-0.703_5	0.35_2	8.10	25.02

[a] Solubility value of Roozeboom (*10*); see text.

Table 2. Properties of Concentrated $CaCl_2(aq)$ from 449 to 523 K Including ΔG° of Reaction from $CaCl_2 \cdot nH_2O(s)$ and S°_{298} for the Solid

			ϕ		$\ln \gamma_\pm$ at				
T/K	P°/bar	$m_{sat}/(mol \cdot kg^{-1})$	exptl	calcd	5 mol·kg^{-1}	m_{sat}	n	$-\Delta_{soln}G^\circ/RT$	$S^\circ_{298}(s)/R$
449	9.1	24.2_5		1.53_5	-0.703_5	0.38_8	1	10.10[a]	16.27
460	11.7	26.6	1.42	1.43_9	-0.929	0.06_2	1	9.35	16.29
449	9.1	26.7_5	1.41	1.45_3	-0.703_5	0.35_2	1/3	11.60	14.10
460	11.7	26.6	1.42	1.43_9	-0.929	0.06_2	1/3	10.73	14.11
473.15	15.5	27.5	1.38	1.39_6	-1.204	-0.29_5	1/3	9.75	14.06
503	27.9	29.6		1.31_4	-1.846	-1.09_2	1/3	7.57	13.86
503	27.9	29.6		1.31_4	-1.846	-1.09_2	0	8.27	12.69
523.15	39.7	30.8_5	1.19_7	1.19_6	-2.296	-1.72_7	0	6.49	12.68

[a] Calculated for the solubility value of CODATA (*3*) for the monohydrate.

questions about the solid actually present in the Roozeboom (*10*) experiment. Sinke et al. (*12*), in the course of a very thorough study of $CaCl_2$ solubility, discovered a new solid hydrate, $CaCl_2 \cdot 1/3H_2O$, which is the equilibrium solid from 460 to 503 K. In the range 449–460 K, the monohydrate is the stable solid, but solutions easily supersaturate and form metastable equilibria with the 1/3 hydrate. Although Roozeboom reports that his experiments from 449 to 473 K related to the monohydrate, his molalities clearly indicate that the equilibria were with the 1/3 hydrate even at 449 K. Consequently, we used Roozeboom's solubility value at 449 K. At 460 and 473 K we used the averages of CODATA and Roozeboom solubilities, the differences being small.

The temperatures, saturation molalities, and experimental osmotic coefficients at m_s are listed in Table 1 for the range of dihydrate stability and in Table 2 for higher temperatures where the number of H_2O in the saturating solid is also stated. At each temperature the parameters a, b, and d of eq 1 were fitted to the ϕ values from HBSM at $m/(mol \cdot kg^{-1}) = 4.75$ and 5.0 and to the experimental ϕ at m_s with $c = -0.0010$ kg^2·mol^{-2} and $e = 2$ throughout. These a, b, and d values were then examined for temperature dependency. Each parameter was quite accurately linear in T from 323 to 423 K and deviated from that linear trend only within the uncertainty at higher temperatures to 473 K. The values for 523 K fell off of this linear trend significantly but not greatly. On the basis of this knowledge, an equation of the following form was chosen for each parameter:

$$f = q_1 + q_2(T/\mathrm{K}) \pm \exp\{(T/\mathrm{K}q_3) - q_4\} \qquad (2)$$

The final term (which can have either sign) is negligible except at temperatures above 423 K and well within the uncertainties even to 473 K. The parameters q_1 and q_2 were determined from data below 423 K, while q_3 and q_4 were selected to fit the value at 523 K exactly and to best agree with other values above 423 K.

On the basis just described and the earlier choices of c and e, the following final expressions are adopted for the parameters in eq 1:

$$a = 8.91_5 - 0.0161(T/\mathrm{K}) + \exp((T/\mathrm{K})/28 - 19.52) \qquad (2a)$$

$$b/(\mathrm{kg \cdot mol^{-1}}) = -0.210 + (5.07 \times 10^{-4})(T/\mathrm{K}) - \exp((T/\mathrm{K})/20 - 30.322) \qquad (2b)$$

$$c/(\mathrm{kg^2 \cdot mol^{-2}}) = -0.0010 \qquad (2c)$$

$$d/(\mathrm{mol^2 \cdot kg^{-2}}) = -73.4 + 0.15(T/\mathrm{K}) - \exp((T/\mathrm{K})/40 - 11.10) \qquad (2d)$$

$$e = 2 \qquad (2e)$$

This completes the expression for the osmotic coefficient for the range $m = 5$ mol·kg^{-1} to saturation molality and for temperature from 323 to 523 K.

The activity coefficient above $m = 5$ mol·kg^{-1} is obtained by integration of the equation

$$\mathrm{d} \ln \gamma_\pm = \mathrm{d}\phi + (\phi - 1)\, \mathrm{d} \ln \mathrm{m} \qquad (3)$$

Substitution of eq 1 with $e = 2$ and integration yield

$$\ln \gamma_\pm(m_2) - \ln \gamma_\pm(m_1) = (a-1)\ln\left(\frac{m_2}{m_1}\right) + 2\mathrm{b}(m_2 - m_1) + \frac{3c}{2}(m_2^{\,2} - m_1^{\,2}) + \frac{d}{2}(m_2^{\,-2} - m_1^{\,-2}) \qquad (4)$$

With $m_1 = 5.0$ mol·kg^{-1}, $\ln \gamma_\pm(m_1)$ is obtained from the HBSM equation, and the other terms in eq 4 are calculated with the parameter values of eq 2.

Tables 1 and 2 list the values of $\ln \gamma_\pm$ at $m = 5$ mol·kg^{-1} and the calculated values from eq 4 for $\ln \gamma_\pm$ at saturation molality. Also shown is the value calculated from eqs 1 and 2 for ϕ at m_s for comparison with the experimental value. And in the next to last column is the value for the change in

Table 3. Osmotic Coefficients (φ) and Activity Coefficients (as $\ln \gamma_\pm$) for $CaCl_2$(aq) at p_{sat}[a]

m/(mol·kg^{-1})	298.15 K	323.15 K	373.15 K	423.15 K	473.15 K	523.15 K
			φ			
0.1	0.856	0.848	0.823	0.785	0.734	0.662
0.2	0.862	0.853	0.824	0.780	0.720	0.638
0.5	0.912	0.900	0.862	0.804	0.726	0.625
1.0	1.041	1.021	0.961	0.878	0.771	0.639
2.0	1.378	1.336	1.223	1.079	0.911	0.724
3.0	1.765	1.693	1.511	1.298	1.067	0.833
4.0	2.178	2.065	1.800	1.507	1.207	0.935
5.0	2.583	2.444	2.077	1.692	1.318	1.013
7.0	3.083	2.831	2.355	1.882	1.429	1.110
10.0		2.901	2.425	1.954	1.511	1.201
15.0				1.909	1.554	1.287
20.0					1.531	1.314
25.0					1.453	1.290
30.0						1.214
			$\ln \gamma_\pm$			
0.1	−0.652	−0.686	−0.787	−0.931	−1.137	−1.449
0.2	−0.745	−0.787	−0.909	−1.088	−1.341	−1.716
0.5	−0.804	−0.857	−1.020	−1.258	−1.591	−2.069
1.0	−0.699	−0.771	−0.988	−1.300	−1.724	−2.312
2.0	−0.235	−0.349	−0.676	−1.124	−1.702	−2.455
3.0	0.378	0.211	−0.243	−0.831	−1.553	−2.437
4.0	1.067	0.834	0.232	−0.508	−1.374	−2.369
5.0	1.777	1.491	0.719	−0.189	−1.204	−2.296
7.0	2.903	2.425	1.417	0.268	−0.960	−2.174
10.0		3.169	1.988	0.670	−0.709	−2.027
15.0				1.008	−0.448	−1.842
20.0					−0.313	−1.727
25.0					−0.280	−1.683
30.0						−1.711

[a] 1 bar for $T/K \leq 373.15$. At $m \leq 4$ and all temperatures the values are calculated from the equations of HBSM. For $T/K > 298.15$ and $m = 5$ the values have been extrapolated from the equation of HBSM. At 298.15 K and $m = 5$ and $m = 7$ the values are from CODATA. All other values are calculated from the equations in this paper.

Gibbs energy $\Delta_{soln}G°$ for the reaction

$$CaCl_2 \cdot nH_2O(s) \rightleftarrows CaCl_2(aq) + nH_2O(l) \qquad (A)$$

with each in its standard state at the given temperature. The equation and other details of the calculation of $\Delta G°$ are given below in connection with the calculations for the properties of the solid hydrates.

For convenience, the following expression can be used for $\ln \gamma_\pm$ at 5 mol·kg^{-1}; it is accurate to 0.004 from 323 to 523 K.

$$Q(T) = \ln \gamma_\pm(m = 5\ \text{mol·kg}^{-1}) = 15.1194 - 0.027793\,(T/\text{K}) - 1502.6/(T/\text{K}) \qquad (5)$$

Then, the expression for the activity coefficient at molalities $m_2 \geq 5$ mol·kg^{-1} becomes

$$\ln \gamma_\pm(m_2) = Q + (a - 1)\ln(m_2/5) + 2b(m_2 - 5) + (3c/2)(m_2^2 - 25) + (d/2)(m_2^{-2} - 1/25) \qquad (6)$$

Table 3 gives the osmotic and activity coefficients for the full range of molality including values from HBSM (*1*) below 5 mol·kg^{-1}. This information is also shown in Figures 3 and 4.

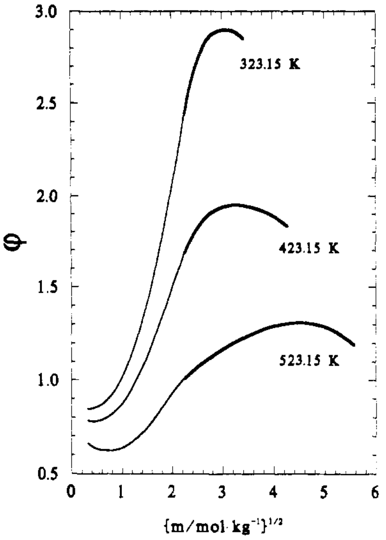

Figure 3. Osmotic coefficient of $CaCl_2$(aq) for the three temperatures indicated. The thin lines to m = 5 mol·kg^{-1} are from HBSM (*1*), while the thick lines at higher m are from this research.

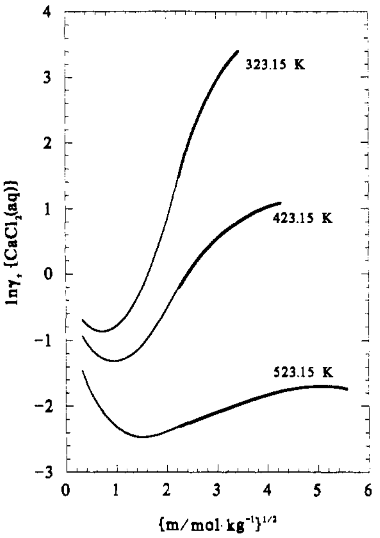

Figure 4. Activity coefficient, as $\ln \gamma_\pm$, of $CaCl_2$(aq) at three temperatures as indicated. Details are as in Figure 3.

The excess Gibbs energy per mole G^E of the aqueous phase in the molality system is

$$G^E/n_2RT = \nu(1 - \phi + \ln \gamma_\pm) \qquad (7)$$

and one combines the results for ϕ and $\ln \gamma_\pm$ with the value $\nu = 3$ for $CaCl_2$ to obtain

$$G^E(m_2)/n_2RT = 3\Big\{(a - 1)[\ln(m_2/5) - 1] + b(m_2 - 10) + \frac{c}{2}(m_2^2 - 75) - \frac{d}{2}(m_2^{-2} + 1/25) + Q\Big\} \qquad (8)$$

where $m_2 \geq 5$ mol·kg^{-1} and m_1 = 5 mol·kg^{-1} have been substituted as appropriate.

The apparent molar relative enthalpy $L\phi$ is just the excess enthalpy and is

$$L\phi/RT = -T[\partial(G^E/n_2RT)/\partial T]_{P,m} \qquad (9)$$

For $T \leq 373$ K, our treatment is at a constant pressure of 1 bar; also the final terms for a, b, and d can be neglected. Then the application of eq 7 to eqs 2 and 6 is straightforward and yields for L at m_2/(mol·kg^{-1})

$$L\phi/RT = 3(T/\text{K})\{0.0161[\ln(m_2/5) - 1] - (5.07 \times 10^{-4})(m_2 - 10) + 0.075(m_2^{-2} + 1/25) - 0.027793 + 1502.6/(T/\text{K})^2\} \qquad (10)$$

The last terms are the temperature derivative of eq 5 which approximates the HBSM for $\ln \gamma_{\pm}$ evaluated at $P = 1$ bar and $m = 5$ mol·kg^{-1}.

Above 373 K, eqs 2a–2d and 5 were generated from data at the saturation pressure of pure water, which is not constant with respect to T, while the derivative in eq 9 is at constant P. Also, the final terms for a, b, and d are no longer negligible. The contributions of these terms are roughly proportional to the saturation pressure; thus, they may represent in part the effect of a pressure increase. An accurate pressure-dependent treatment requires volumetric data for the system at the high molalities and temperatures of interest, and we are not aware of such data for $CaCl_2$(aq). Thus, we can only offer eq 10, either with or without the derivatives of the final terms for a, b, and d, as an estimate that should be a reasonable approximation to at least 398 K.

There are enthalpy-of-dilution measurements from 7.3 to 5.8 mol-kg^{-1} at 73 bar from HBSM (*1*). Comparisons are subject to an unknown pressure correction, but it is probably small below 423 K. The agreement with the value from eq 10 is essentially perfect at 373 K and within 3% at 348 K. As one approaches the lowest temperature to which the Gibbs energy was fitted, one expects a larger deviation in the calculated enthalpy. When this aspect is considered, the agreement is also satisfactory at 323 K. The uncertainties in comparisons at temperatures above 373 K have been discussed above.

For the range where enthalpy as well as Gibbs energy are known, the excess entropy is also available. Also, the temperature derivative of the apparent molar enthalpy yields the relative heat capacity (which is equal to the excess heat capacity). But results based on a second derivative of eq 8, the excess Gibbs energy, will have large uncertainties.

Properties of Solid $CaCl_2$ and Its Hydrates and Their Equilibria with Aqueous $CaCl_2$. Values are given in Tables 1 and 2 for the change in Gibbs energy $\Delta G°/RT$ for the solution reaction

$$CaCl_2{\cdot}nH_2O(s) = CaCl_2(aq) + nH_2O(l)$$

at various temperatures. These are given by the equation

$$\Delta G°/RT = 3 \ln m + 2 \ln 2 + 3 \ln \gamma_{\pm} + n \ln a_{H_2O} \quad (11)$$

with

$$\ln a_{H_2O} = -\nu m \phi/\Omega \quad (11a)$$

For this case $\nu = 3$, while m, ϕ, and $\gamma_{\pm}$ are all for the saturated solution, and Ω is the number of moles, 55.51, of water per kilogram. The value of $\Delta G°$ is for the saturation pressure in each case. We next relate these values to the properties of the various crystal hydrates at 298.15 K.

Consider first the relationship at constant pressure P_r, the saturation pressure at the reaction temperature T_r. Standard thermodynamics gives the equation

$$-\left(\frac{\Delta G°}{RT}\right)_{T_r} = \frac{\Delta S°_{298}}{R} - \frac{\Delta H°_{298}}{RT_r} + \int_{298}^{T_r}\left(\frac{\Delta C_p°}{R}\right)\left(\frac{1}{T} - \frac{1}{T_r}\right)\mathrm{d}T \quad (12)$$

Table 4. Equilibrium Pressures and Values of $\Delta_r S_{298}$ for Reaction B[a] Calculated from Eq 14

T/K	P/Torr	$\Delta_r S_{298}/R$	source
321.9_0	4.58	14.08	S
332.6_5	8.44	14.07	S
344.8_5	15.9	14.05	S
352.6_5	23.3	14.04	S
364.4_5	39.9	14.02	S
$373._{15}$	60	14.0_4	R
375.0_5	63.5	14.01	S
386.5_5	101.1	13.99	S
$402._{15}$	175	13.9_3	R
$428._{15}$	438	13.9_3	R
$438._{15}$	607	13.9_5	R
$443._{15}$	715	13.9_4	R
$448._{65}$	842	13.9_4	R

[a] $CaCl_2{\cdot}2H_2O(s) \rightleftarrows CaCl_2{\cdot}H_2O(s) + H_2O(g)$.

The heat capacity of $CaCl_2$(aq) at P_r was taken from the equation of HBSM (*1*). For liquid water and a solid the pressure correction is negligible; also, the heat capacity of water is well known from many sources. For $CaCl_2$(s), Moore (*13*) gives an equation valid from 298 to 1055 K. Few data are available for $CaCl_2$ hydrates, but Pabalan and Pitzer (*14*) examined data for other similar hydrates including $MgCl_2{\cdot}nH_2O$ and $MgSO_4{\cdot}nH_2O$ at 298 K and found that the heat capacity increases by very nearly $5R$ per H_2O for these series. Since the heat capacity of liquid H_2O is close to $9R$, the value of $\Delta C_P°$ in eq 12 increases by $4R$ per H_2O from that for anhydrous $CaCl_2$(s). The change with temperature in this quantity is small, and the temperature factor in eq 12 decreases very rapidly with an increase in T. Also at the high temperatures, the number of H_2O in the saturating hydrate is small, only 1/3 above 449 K; hence, the addition to $\Delta C_P°$ for H_2O of hydration was taken to be constant with respect to T. Thus, one has for substitution in eq 12 the expression

$$\Delta C_P°/R = C°_{P,aq}/R + 4n - 8.645 - 0.00153(T/\mathrm{K}) + 3.0 \times 10^4/(T/\mathrm{K})^2 \quad (13)$$

where $C°_{P,aq}$ is calculated from HBSM (*1*) and the last three terms for $CaCl_2$(s) are from Moore (*13*).

For $\Delta_{soln}H°$(298 K), the enthalpy of solution for hydrates with $n = 2$, 1, and 1/3 as well as the anhydrous $CaCl_2$, we use the appropriate differences in values of $\Delta_f H°$ from CODATA (*3*) which are given in Table 6. These are essentially the enthalpies of solution measured by Sinke et al. (*12*). But for the entropies of the solids there are large uncertainties in any values from other sources. We have, however, from Tables 1 and 2, the values of $\Delta_{soln}G°/RT$. Then, we solve eq 12 at each temperature for $\Delta_{soln}S°_{298}$. Next, we calculate $S°_{298}$ for the solid from the values of $S°_{298}$ of $6.856R$ for $CaCl_2$(aq) and $8.413R$ for H_2O(l), both taken from CODATA (*3*). In principle, pressure corrections should be made for $\Delta_{soln}S_{298}$ and $\Delta_{soln}H_{298}$, but the volume change on solution at 298 K is only −34 cm^3·mol^{-1} and the effect is far less than experimental uncertainty, even with the highest $P_r = 39.7$ bar for 523 K.

The resulting values for $S°_{298}/R$ for the various solids are given in Tables 1 and 2 in the last column. The values related to a given solid should be constant and are within reasonable uncertainties.

In addition to the vapor pressures of the saturated solutions in equilibrium with the crystalline solids, there are measurements of the vapor pressure of H_2O in equilibrium with two solids. For example,

$$CaCl_2{\cdot}2H_2O(s) \rightleftarrows CaCl_2{\cdot}H_2O(s) + H_2O(g) \quad (B)$$

$$(3/2)CaCl_2{\cdot}H_2O(s) \rightleftarrows (3/2)CaCl_2{\cdot}(1/3)H_2O(s) + H_2O(g) \quad (C)$$

Note that in these cases gaseous water is the product, whereas liquid H_2O was shown for reaction A.

In general, it is more difficult to obtain true equilibrium pressures for two solids as compared to the case of a liquid solution plus a solid, and we have not considered data of uncertain validity. Dr. G. C. Sinke (*15*) has made available to us unpublished measurements for reactions B and C. Equilibrium was approached from both higher and lower pressures. These results are shown in Tables 4 and 5. For

Table 5. Equilibrium Pressures and Values of Δ_rS_{298} for Reaction C[a] Calculated from Eq 14

T/K	P/Torr	Δ_rS_{298}/R	source
386.5_5	26.7	19.35	S
398.5_5	51.0	19.32	S
411.5_3	102.6	19.34	S
423.5_5	192.6	19.37	S
433.5_3	309.5	19.38	S

[a] $(3/2)CaCl_2{\cdot}H_2O(s) \rightleftarrows (3/2)CaCl_2{\cdot}(1/3)H_2O(s) + H_2O(g)$.

Table 6. Summary of Thermodynamic Properties at 298.15 K

substance	$-\Delta_fH°$/ (kJ·mol^{-1})	$S°/R$	$-\Delta_fG°$/ (kJ·mol^{-1})
$CaCl_2(s)$	795.39 ± 0.3[a]	12.6_8 ± 0.3[c]	747.9_1 ± 0.8[c]
$CaCl_2{\cdot}(1/3)H_2O(s)$	901.07 ± 0.3[a]	14.0 ± 0.3[c]	833.8 ± 0.8[c]
$CaCl_2{\cdot}H_2O(s)$	1110.83 ± 0.3[a]	16.2 ± 0.2[c]	1002.7 ± 0.6[c]
$CaCl_2{\cdot}2H_2O(s)$	1403.9_7 ± 0.3[a]	24.8_0 ± 0.2[b,c]	1247.4 ± 0.6[b,c]
$CaCl_2{\cdot}4H_2O(s)$	2009.6_0 ± 1.0[b]	37.2_0 ± 0.3[b]	1733.6 ± 1.0[b]
$CaCl_2{\cdot}6H_2O(s)$	2609.9_4 ± 0.1[b]	41.1_1 ± 0.2[b]	2215.6_6 ± 0.5[b]
$CaCl_2$(aq,std state)	877.16[a]	6.856[a]	815.24[a]
$H_2O(l)$	285.83[a]	8.413[a]	237.14[a]
$H_2O(g)$	241.83[a]	22.712[a]	228.58[a]

[a] Values from CODATA (*3*) [b] Values from Pitzer and Shi (*2*). [c] Values from this research.

reaction B the old measurements of Roozeboom (*10*) agree within their lower precision and are included in Table 4 for 373 K and higher temperatures.

In treating the data for reactions B and C, we approximate the heat capacity of $H_2O(g)$ as $4R$, whereupon ΔC_P for each reaction is $-R$. Then we follow the same method used above with eq 12 and obtain

$$\ln f = \frac{\Delta_rS°_{298}}{R} - \frac{\Delta_rH°_{298}}{RT_r} - \ln\left(\frac{T_r/K}{298.15}\right) + 1 - \frac{298.15}{T_r/K} \qquad (14)$$

where P is converted from the values originally reported in Torr to fugacities in bars. Again, we take the $\Delta_rH°_{298}$ to be accurately known from Sinke et al. (*12*) as adopted by CODATA (*3*) and solve eq 14 for $\Delta_rS°_{298}/R$. The results are given in Tables 4 and 5 together with the source of each measurement, R for Roozeboom (*10*) and S for Sinke (*15*). In each table the Δ_rS_{298} values are constant well within the absolute uncertainty, although there is a small trend downward with an increase in temperature in Table 4.

The entropy values for the $n = 2$, $n = 1$, and $n = 1/3$ hydrates in Tables 1 and 2 and the ΔS values involving these hydrates in Tables 4 and 5 are all consistent well within their absolute uncertainties. There is little basis for assigning precise uncertainties to each value; hence, no formal regression was made. The best values of the entropies were selected with consideration of various aspects according to our best judgement. These are given in Table 6, along with various other thermodynamic properties taken from CODATA (*3*) or the previous paper in this series (*2*). The values for the dihydrate are unchanged, although the uncertainties in entropy and Gibbs energy are reduced a little. The good agreement related to the $n = 1$ and $n = 1/3$ hydrates from the different approaches justifies a smaller uncertainty than would have been estimated from either method taken alone.

The entropy of anhydrous solid $CaCl_2$ merits further discussion. There are good heat capacity measurements above 50 K from Kelley and Moore (*16*), but the extrapolation below that temperature is uncertain. Kelley and Moore estimate S_{50} to be $2.30R$ and with $S_{298} - S_{50} = 11.3_6R$ obtained the value $S_{298} = 13.6_6R$, which is larger than our result of 12.6_8R by substantially more than our estimated uncertainty.

Subsequent to the work of Kelley and Moore, heat capacity measurements were made for $SrCl_2$ (*17*) and $BaCl_2$ (*18*); they extend to much lower temperature and indicate that the earlier extrapolation for $CaCl_2$ was considerably too large. Also, although $MgCl_2$ was only measured (*16*) to 50 K, the effect of the decrease in atomic mass from Ca to Mg implies a smaller and more certain extrapolation. Figure 5 shows a comparison of the entropies at 50 K for these substances. For this low-temperature range, it is the total formula mass of the salt that is most relevant; consequently, that mass is taken as the variable for comparison.

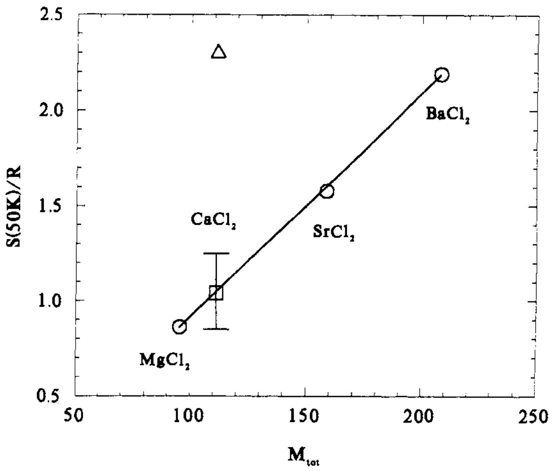

Figure 5. Entropies at 50 K for several MCl_2 solids as a function of the molecular mass M. The triangle shows the original estimate of Kelley and Moore (*16*) for $CaCl_2(s)$, while the square indicates our revised estimate together with its uncertainty.

A reasonable curve through the values for $MgCl_2$, $SrCl_2$, and $BaCl_2$ in Figure 5 indicates a value of $(1.0_5 \pm 0.2)R$ for S_{50} for $CaCl_2$. The uncertainty of $0.2R$ for $CaCl_2$ arises primarily from the uncertainty estimated for $MgCl_2$. Then adding the experimental value of 11.3_6R for $S_{298} - S_{50}$ from Kelley and Moore, one obtains $(12.4_1 \pm 0.5)R$ for S at 298.15 for $CaCl_2(s)$. The agreement with the value $(12.6_8 \pm 0.3)R$ derived from the treatment above in this paper is excellent.

This need for revision of the extrapolation for $CaCl_2$ was noted by Stull and Prophet (*19*), who chose $1.2R$ for S_{50}; this agrees with both of our values within their uncertainties. Garvin et al. (*3*) also revised downward the extrapolation for $CaCl_2(s)$ but chose $S_{50} = 1.7R$, which appears from Figure 5 to be still too large a value.

While the entropies in Table 6 for the various hydrated crystals appear to be well determined within the indicated uncertainties, the differences per H_2O are less regular than was noted for the $MgCl_2{\cdot}nH_2O$ series [see Pabalan and Pitzer (*14*)]. From this comparison, the entropies of the $n = 2$ and $n = 4$ hydrates of $CaCl_2$ are larger than expected and the values for $n = 1$ and $n = 6$ are smaller. A similar situation exists for the ranges of stability of successive hydrates in equilibrium with saturated solution. For $MgCl_2$ the $n = 6$, $n = 4$, and $n = 2$ hydrates are successively the stable solid over similarly long temperature ranges (more than 60 K in each case). In contrast $CaCl_2{\cdot}4H_2O$ is the stable solid for only 16 K (302.85–318.55 K), while both the hexahydrate and the dihydrate have large stability ranges of over 75 K each.

Comparison of structures in crystals also shows a difference between the $MgCl_2{\cdot}nH_2O$ and $CaCl_2{\cdot}nH_2O$ series. For the magnesium series the coordination number of the Mg^{2+} ion appears to remain constant at 6. The structure of the hexahydrate has six H_2O's around Mg, while there are six Cl's around Mg in $MgCl_2$. For the $CaCl_2$ series the coordination number of the Ca^{2+} ion is larger and ranges from 6 to 10. As discussed by Phutela and Pitzer (*5*), there is considerable variability in the structural pattern for the intermediate hydrates of $CaCl_2$. While this structural variability may eventually explain the irregularity in entropy increments per H_2O, it must be left as an interesting question at this time.

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