

Thermodynamics of Calcium Chloride in Highly Concentrated Aqueous Solution and in Hydrated Crystals

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Measured values of the pressure of H₂O over saturated solutions in equilibrium with the dihydrate, tetrahydrate or hexahydrate of CaCl₂ are converted to osmotic coefficients and compared with literature values for solutions of smaller molality. It is found that the osmotic coefficient is constant, within the uncertainty, from about 7 mol·kg⁻¹ to saturation at all temperatures from 25 to 100°C. From this simple approximation, the activity coefficient is calculated for high molalities and at saturation. By combination of these results with other established data, entropies and Gibbs energies of formation are calculated for the crystalline hydrates of CaCl₂.

KEY WORDS: Calcium chloride; activity coefficient; osmotic coefficient; thermodynamics

1. Introduction

There are many good measurements of the thermodynamic properties of CaCl₂ in aqueous solution, but the representation of the full range of these data by an equation has proven to be very difficult. Recently, two relatively comprehensive treatments have been presented, one by Ananthaswamy and Atkinson⁽¹⁾ (AA) and the other by Garvin *et al.*⁽²⁾ in a special CODATA volume. In neither case is the equation valid to saturation molality above about 40°C, and in each case it is clear that an extrapolation to higher molality will lead to gross error. Even within the saturation molality of 7.29 mol·kg⁻¹ at 25°C an ion- interaction treatment requires terms through sixth⁽¹⁾ or seventh⁽²⁾ order interactions. The usual treatment through the third order, which suffices to saturation for MgCl₂ and similar salts, fails above 4.5 mol·kg⁻¹ for CaCl₂.⁽³⁾ Our first

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aim is an expression for the properties of $\text{CaCl}_2(\text{aq})$ valid to saturation molality and to 100°C .

The properties of the saturated solution are, of course, related to those of the saturating solid. The solid is the hexahydrate, the tetrahydrate, or the dihydrate crystal with stability ranges of increasing temperatures from 25 to 100°C . Unfortunately, the thermodynamic properties of these crystals are not known accurately enough to help determine the solution properties. Indeed, some of the properties given by Garvin *et al.*⁽²⁾ are inconsistent with the known stability ranges of these hydrated crystals. Thus, it is a second objective to determine best values for the Gibbs energies, enthalpies, and entropies for these hydrates of CaCl_2 .

2. Data and Equation for the Liquid Solution Phase

The CODATA⁽²⁾ and AA⁽¹⁾ reports include full lists of references for solution properties in the unsaturated range. Figure 1 shows for three temperatures the curves for the osmotic coefficient ϕ from the equations developed by CODATA and AA. At 25°C there were measurements of very high precision and earlier equations which are accurately reproduced in the new studies. At higher temperatures the data are less accurate, less complete, and not fully consistent, especially for high molalities. The difference between the AA and CODATA curves, which was negligible at 25°C , becomes significant and is indicative of the uncertainty for either equation. We have chosen to adopt as a working basis the CODATA values, which are the more recent, but to assume that significant deviation toward the AA curves is reasonable.

Values for the water vapor pressure over saturated solutions are given by Collins and Menzies,⁽⁴⁾ Lannung,⁽⁵⁾ and Roozeboom.⁽⁶⁾ The first and second are more recent and agree very well. Roozeboom's measurements are much older and presumably less accurate but are still in reasonable agreement. Table I shows the osmotic coefficients calculated from these vapor pressures and the saturation molalities given by CODATA. In the seventh column are the values adopted for further calculations; except at 29°C , they are the means of the values of Collins and Menzies⁽⁴⁾ and Lannung⁽⁵⁾ or those of the former at the higher temperatures. At 29°C , only slightly above 25°C and with a saturation molality of only $8.73\text{ mol}\cdot\text{kg}^{-1}$, we preferred the CODATA⁽²⁾ value.

These values of the osmotic coefficient at saturation molality, which rises to $13.6\text{ mol}\cdot\text{kg}^{-1}$ at 100°C , are remarkably nearly equal to the values in the range 7 to 8 molal at each temperature. One also notes that ϕ at 25°C is almost exactly constant over the range 8 to 9 molal and

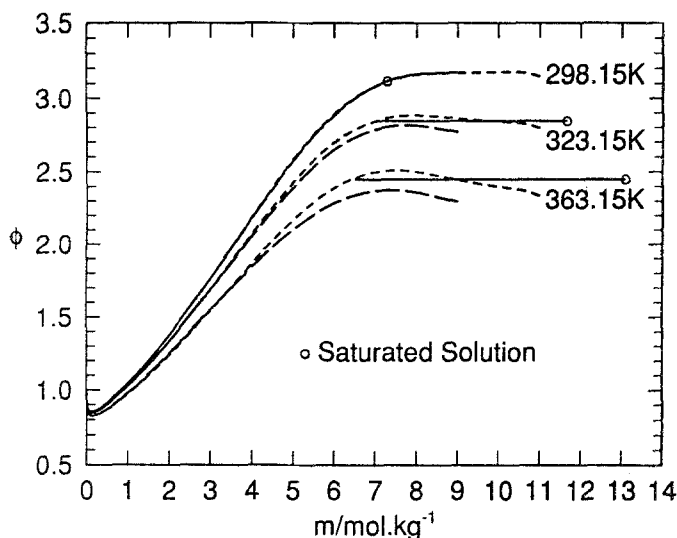


Fig. 1. The osmotic coefficient of $\text{CaCl}_2(\text{aq})$. Circles are values for the saturated solution from Table I, solid or short-dashed curves are from Ref. 2, long-dashed curves are from Ref. 1, straight lines connect circles to CODATA curves.

possibly to 10 molal. This surprising constancy of the osmotic coefficient in the concentrated range was noted by Jakli and Van Hook,⁽⁷⁾ who wrote, "The concentration dependence of $\phi(\text{CaCl}_2)$ is interesting. It rises smoothly up to 6 or 7 molal and then rather abruptly flattens to an apparently constant value." They recommend that values at 8 molal be taken as estimates for higher molality and show such values up to 10 molal in their table. We find this concept valid over the full range to saturation molality and adopt it for further calculations.

The range of constant ϕ is assumed to begin at m_1 and extend to the saturation molality m_{sat} . The Gibbs-Duhem equation for a two-component system may be written in the form

$$d \ln \gamma_{\pm} = d\phi + (\phi - 1)d \ln m \quad (1)$$

Thus, if ϕ is constant, one obtains a very simple expression for the activity coefficient at any molality m greater than m_1

$$\ln \gamma_{\pm}(m) = \ln \gamma_{\pm}(m_1) + (\phi - 1) \ln(m/m_1) \quad (2)$$

For calculations of the activity coefficient at molalities above m_1 , we use the adopted value of ϕ_{sat} and select a value of m_1 , where ϕ from CODATA is very close to ϕ_{sat} . Then the value of $\ln \gamma_{\pm}(m_1)$ from

Table I. Properties of Concentrated Aqueous CaCl_2 Solutions

T (K)	m_{sat}	ϕ_{sat}					m_1	$\ln \gamma_{\pm}$ (m_1)	$\ln \gamma_{\pm}$ (m_{sat})
		C.M.	Lann.	Roos.	CODATA	Adopt.			
302.85	8.73	3.13	3.10 ₅	3.15	3.111	3.111			3.36 ₀
313.15	10.10	3.04 ₅	3.02 ₇	3.06	2.97	3.03	9.00	3.17 ₀	3.40 ₄
318.55	11.54	2.94 ₅	2.89 ₅	2.92		2.92	7.00	2.53 ₄	3.49 ₄
323.15	11.65	2.84 ₈	2.84 ₂	2.83		2.84 ₅	7.00	2.44 ₂	3.38 ₂
333.15	11.95	2.75 ₀		2.67		2.75	7.00	2.25 ₇	3.19 ₂
343.15	12.2 ₀	2.67 ₀		2.57		2.67	7.00	2.06 ₇	2.99 ₅
353.15	12.6 ₅	2.55 ₃		2.44		2.55	6.75	1.80 ₀	2.77 ₄
363.15	13.1	2.44 ₈		2.34		2.45	6.50	1.53 ₃	2.54 ₉
373.15	13.6	2.34 ₉		2.25		2.35	6.25	1.26 ₄	2.31 ₄

CODATA⁽²⁾ is inserted into Eq. (2). With the values of ϕ_{sat} , m_1 , and $\ln \gamma_{\pm}(m_1)$ in Table I, the calculation of $\ln \gamma_{\pm}(m)$ is so simple that there is no need for a general table, but the values for $\ln \gamma_{\pm}(m_{\text{sat}})$ are given in the last column of Table I.

The finite change in slope of the ϕ vs. m curve at m_1 in Fig. 1 is, of course, unphysical. One could avoid this by taking an appropriate linear combination of the AA and CODATA functions to obtain a zero slope at the level of $\phi(m_{\text{sat}})$. But any practical use of different expressions for the two ranges of molality will leave a discontinuity of a higher derivative, if not of the first. One notes from Eq. (1) that the integral over the full range of m gives just Eq. (2) without any contribution from a change in $d\phi/dm$ at m_1 ; hence, there is no practical need to complicate the treatment to avoid this discontinuity.

While the simple assumption of constant ϕ in the high molality range introduces uncertainty into calculated values from Eq. (2), the uncertainty in $\ln \gamma_{\pm}(m_1)$ is probably greater. Thus, the difference between the AA⁽¹⁾ and CODATA⁽²⁾ values of $\ln \gamma_{\pm}(m_1)$ can be taken as an estimate of the uncertainty in $\ln \gamma_{\pm}$ at higher m ; this difference varies with T and m_1 from 0.11 at 40°C, $m_1 = 9.0$, to 0.08 at 50°C, $m_1 = 7.0$, and to 0.15 at 90°C, with $m_1 = 6.5$.

From crystal structures⁽⁸⁾ and other evidence, we know that Ca^{2+} coordinates up to 8 or 9 water molecules in preference to chloride ions. Thus, below 6 molal essentially all Ca^{2+} ions can be fully surrounded by water molecules associated with a single calcium ion. But at higher molality the pattern must change, with some chloride ions in direct contact with calcium ions and possibly some water molecules shared between calcium ions. Thus, the strong curvature of the osmotic coef-

Table II. Thermodynamic Properties Derived from the
Values in Table I

n	T/K	$-(\Delta G_T^0/RT)$	$S_{298}^0(\text{cr})/R$	$-\Delta_f G_{298}^0(\text{cr})^a$
6	298.15	9.04 ₂	41.11	2215.6 ₆
6	302.85	9.16 ₁	41.10	2215.6 ₄
4	302.85	12.09 ₆	32.73	1733.6 ₃
4	313.15	11.91 ₉	32.74	1733.6 ₆
4	318.55	11.93 ₉	32.64 ₅	1733.4 ₂
2	318.55	15.56 ₃	24.98	1247.8 ₉
2	323.15	15.31 ₅	24.96	1247.8 ₃
2	333.15	14.85 ₂	24.83 ₅	1247.5 ₂
2	343.15	14.35 ₄	24.75	1247.3 ₂
2	353.15	13.83 ₄	24.70	1247.1 ₉
2	363.15	13.28 ₁	24.68	1247.1 ₄
2	373.15	12.70 ₃	24.69 ₅	1247.1 ₈

^a Units, kJ·mol⁻¹.

ficient in the 5.5 to 8 molal range is to be expected, and a decrease in curvature above 8 molal is reasonable. The very near constancy of ϕ from 8 to saturation molality is surprising, however, and presumably involves an accidental cancellation of tendencies toward upward and downward curvature.

3. Properties of Crystalline Hydrates

After one of us called attention in 1988 to the inconsistencies in the CODATA⁽²⁾ values for the Gibbs energy of formation $\Delta_f G^0$ for the 4, 2, and 1 hydrates, Garvin carefully re-evaluated various data and provided an improved set of values, together with details concerning their selection.⁽⁹⁾ We accept these values for $\Delta_f H_{298}^0$ for the 6, 4, and 2 hydrates which concern us here, together with $\Delta_f G_{298}^0$ and S_{298}^0 for the 6 hydrate; these are presented, with Garvin's approval, in our summary. For the 4 and 2 hydrates, however, better values of S^0 and thereby of $\Delta_f G^0$ can now be obtained from the properties of the saturated solution. This calculation requires estimates for the heat capacity of the crystalline hydrates, since direct measurements are not available. This problem was studied by Pabalan and Pitzer⁽¹⁰⁾ for a variety of other salt hydrates including those of MgCl_2 , and they concluded that each mole

of H_2O increased the heat capacity by about 5R. This assumption can be combined with information in the CODATA report⁽²⁾ for anhydrous $\text{CaCl}_2(\text{cr})$, $\text{H}_2\text{O}(\text{l})$, and $\text{CaCl}_2(\text{aq})$ to yield ΔC_p° for the reaction



The $\Delta_f H_{298}^\circ$ values revised from CODATA by Garvin,⁽⁹⁾ together with further data in the CODATA report,⁽²⁾ yield ΔH_{298}° for the reaction for each n , while $\Delta_f G^\circ(T)$ can be calculated from the activity and osmotic coefficients for the saturated solution (Table I). Starting with the ΔG° of reaction at each temperature, other data can be combined by standard thermodynamic equations to yield S_{298}° and $\Delta_f G_{298}^\circ$ for the hydrate in equilibrium with saturated solution at that temperature. At 29°C, values are obtained for both the 6 and 4 hydrates and at 45°C for both the 4 and 2 hydrates. These results are shown in Table II. The agreement of values calculated for a given hydrate from data for different temperatures is excellent. Even for the wide temperature range 45 to 100°C for the dihydrate, the differences among values of S_{298}° or $\Delta_f G_{298}^\circ$ are less than the uncertainty for the assumed $\Delta_f H_{298}^\circ$ or for $\ln \gamma_\pm(m_1)$.

Table III. Summary of Thermodynamic Properties at 25°C

Substance	S°/R	$-\Delta_f G^{oa}$	$-\Delta_f H^{oa}$
$\text{CaCl}_2(\text{aq, std. state})^b$	6.856	815.24	877.16
$\text{CaCl}_2(\text{cr})^b$	13.034	748.79	795.39
$\text{H}_2\text{O}(\text{l})^b$	8.413	237.14	285.83
$\text{CaCl}_2 \cdot 2\text{H}_2\text{O}(\text{cr})$	$24.8_0 \pm 0.3^d$	1247.4 ± 0.7^d	$1403.9_7 \pm 0.5^c$
$\text{CaCl}_2 \cdot 4\text{H}_2\text{O}(\text{cr})$	$32.7_0 \pm 0.3^d$	1733.6 ± 1.0^d	$2009.6_0 \pm 1.0^c$
$\text{CaCl}_2 \cdot 6\text{H}_2\text{O}(\text{cr})$	$41.1_1 \pm 0.2^{c,d}$	$2215.6_6 \pm 0.5^{c,d}$	$2609.9_4 \pm 0.1^c$

^a Units: $\text{kJ} \cdot \text{mol}^{-1}$. ^b Values from Ref. 2 taken as exact for further calculations. ^c Values from Ref. 9 (revised from CODATA). ^d Values from this research.

Averaged values from Table II are given in Table III, together with the values from Garvin⁽⁹⁾ and from CODATA⁽²⁾ which were used in our calculations or are of interest for other calculations. The values in the first three lines from CODATA were taken as exact for the present calculations; for more general calculations the uncertainties given by CODATA⁽²⁾ should be considered. The values for $\Delta_f H_{298}^\circ$ from Garvin⁽⁹⁾ were taken as exact for our calculations, but in this case the uncer-

tainties are shown in Table III and were considered for the uncertainties assigned to the new values of S° and $\Delta_f G^\circ$. For some other calculations, these uncertainties must be increased to include those of the CODATA values taken to be exact.

The values given by Eq. (2) with Table I and those of Table III should be valuable for various problems involving CaCl_2 in hydrate crystals or in concentrated solution.

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