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Correlations

Solid−Liquid Equilibrium in the System of $CaCl_2-H_2O$ with Special Regard to the Transition Points

Jaroslav Pátek,* Jaroslav Klomfar, and Monika Součková

Institute of Thermomechanics, v.v.i., Academy of Sciences of the Czech Republic,
Dolejškova 5, CZ 182 00 Prague 8, Czech Republic

Experimental data on the $T-x$ and $p-T$ solid−liquid equilibrium relations of the $CaCl_2-H_2O$ system have been used simultaneously to determine temperatures, pressures, and solution compositions at the transition points between calcium chloride hydrates. The (T, p, x) coordinates of the transition points have been determined from intersections of the curves corresponding to the adjacent hydrate branches of the SLE phase diagram in the $T-x$ and $p-x$ planes. For this purpose, a set of empirical temperature−molar fraction and pressure−molar fraction expressions has been developed describing the solid−liquid equilibrium relations of the $CaCl_2-H_2O$ system. The equations for the $T-x$ relation cover the full composition range while the equations describing the $p-x$ relation cover compositions up to the salt mole fraction of $x = 0.35$ (i.e., mass fraction of $w = 0.77$), corresponding to the transition from one-third hydrate to anhydrate. Equations of a special structure were used, involving the coordinates of the transition points as parameters, which makes possible their direct nonlinear optimization via least-squares fits to experimental data. The estimates of uncertainties in the obtained values of the coordinates of the transition point range from 0.1 K to 5 K for temperatures and from $1 \cdot 10^{-4}$ to $1.6 \cdot 10^{-3}$ for solution composition expressed in salt mole fraction.

Introduction

The properties of the phase diagram of the condensed aqueous system of calcium chloride are of interest in a wide variety of fields similarly to those of aqueous systems of alkali halides.[1] Commercial applications of calcium chloride and its hydrates exploit one or more of its properties with regard to aqueous solubility, hygroscopic nature, and the heat gained or lost when one hydrate changes to another. Calcium chloride hexahydrate is used as a thermal energy storage medium. Aqueous solutions of calcium chloride is suited for use as a desiccant in sorption based air conditioning equipment. As the anhydrous calcium chloride is manufactured in a large scale by the evaporation of brines, knowledge of the path of dehydration is important to minimize the required energy.

Studies on the explicit description of the solid−liquid equilibrium diagram of the $CaCl_2-H_2O$ system including the transition points between hydrates are scarce. Experimental data on the transition point coordinates are contained in the literature.[2−7]

Voigt[8] used the modified BET model according to Stokes and Robinson[9] to describe the liquidus curves of the hydrates of $CaCl_2-H_2O$ in the $T-x$ diagram. He presented no explicit expressions describing the curves in his paper.

Zeng et al.[10] published empirical solubility−temperature equations for the hexahydrate, the three modifications of the tetrahydrate, and for the dihydrate of the $CaCl_2-H_2O$ system. The existence of the eutectic point and the transition points are not explicitly taken into account in the study.

Conde[11] gave a description of the solid−liquid equilibrium curve of the $CaCl_2-H_2O$ system in the form of a functional dependence of the temperature on the mass fraction.

The aim of the present study was to determine systematically the (T, p, x) coordinates of the eutectic point and the transition points between hydrates in the $CaCl_2-H_2O$ system and to provide a reliable description of its solid−liquid coexistence curves in the $T-x$ and $p-x$ planes based on critically evaluated experimental data compiled from the literature.

Two-Solid Saturation Points

In equilibrium with a saturated solution, the solid phase of the $CaCl_2-H_2O$ system is formed by ice on the low concentration side, by hydrates with 6, 4, 2, 1, and $^1/_3$ mol of water per 1 mol of salt as the salt concentration in the solution increases, and by anhydrous salt at the highest concentrations. The existence of the one-third hydrate was revealed by Sinke et al.[12] as late as 1985. In addition, there exist three different crystalline modifications of tetrahydrate denoted as α, β, and γ. A note of caution is in order here as there is some confusion in the literature concerning the tetrahydrate modifications. It stems from the fact that the present-day γ-$CaCl_2 \cdot 4H_2O$ was originally assigned by Roozeboom[3] as β-$CaCl_2 \cdot 4H_2O$ in 1889. In 1933, Basset et al.[13] found a new solubility line lying between that of α-$CaCl_2 \cdot 4H_2O$ and Roozeboom's β-$CaCl_2 \cdot 4H_2O$. Basset assigned Roozeboom's β-$CaCl_2 \cdot 4H_2O$ as γ-$CaCl_2 \cdot 4H_2O$ and the new curve for β-$CaCl_2 \cdot 4H_2O$.

The solid−liquid phase diagram of the system thus consists of branches corresponding to the particular hydrates separated either by an eutectic or by a peritectic point, where two solids are precipitating simultaneously (Figures 1 and 2).

To determine the transition temperatures between hydrates and the corresponding saturated solution compositions, thermal analysis is used or the transition points are fixed by intersection of extrapolated curves for hydrates. The published data on the coordinates of the two-solid points of the $CaCl_2-H_2O$ system are much more scarce than those of such salt−water systems as $LiCl-H_2O$ or $LiBr-H_2O$.[1] Table 1 gives an overview of the results of studies on the two-solid points. In the table, the temperatures are given in degrees Celsius in order not to confuse by the conversion to kelvin the number of significant figures as it was stated by particular

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* Corresponding author. Phone: +420 266053153. Fax: +420 28584695. E-mail: patek@it.cas.cz.

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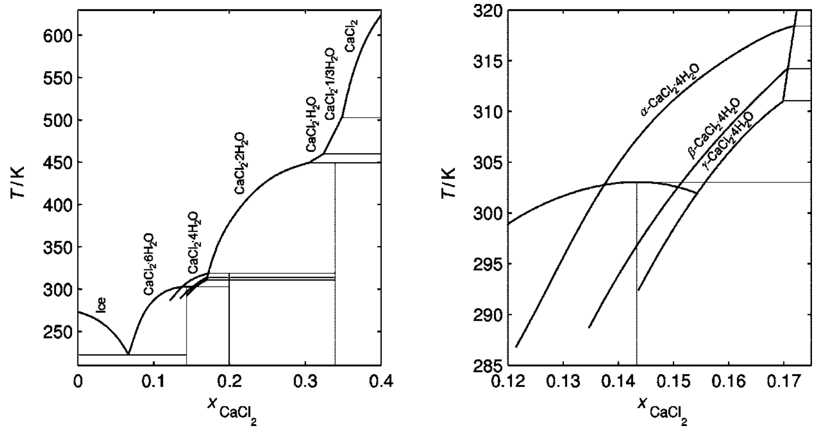

Figure 1. SLE phase diagram for the binary system $CaCl_2-H_2O$; temperature T as a function of the salt mole fraction x_{CaCl_2}.

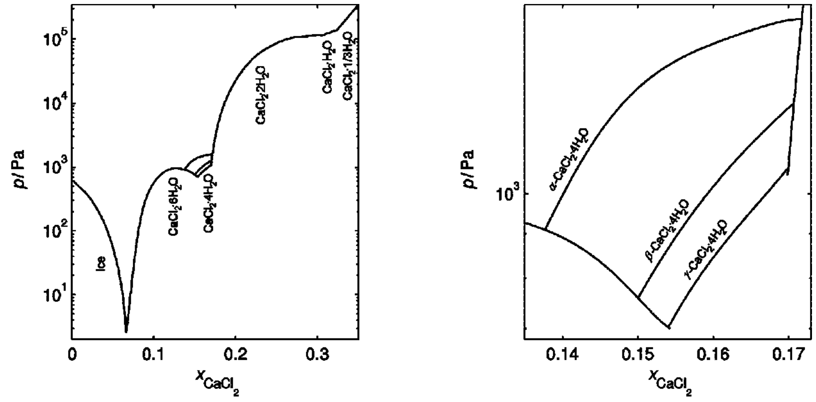

Figure 2. SLE phase diagram for the binary system $CaCl_2-H_2O$; pressure p as a function of temperature T.

authors. Data found in the literature are conflicting. Determinations of the transition temperatures show greater discrepancies than would be expected from the estimated precision of individual determinations. The coordinates of the two-solid points obtained by various authors are scattered over the interval of the width of the order of several kelvin for temperature and of the order of 0.001 for composition expressed in salt mole fraction. The thermal analysis seems not to provide much more reliable results than the data obtained by extrapolation.

Data Selection

Within the present study, 58 experimental studies have been collected containing a total of 569 data points on the $T-x$ solid−liquid equilibrium relation of the $CaCl_2-H_2O$ system and 7 published studies containing 139 data points concerning its $p-T$ relation. A body of 416 and 128 of them, respectively, were selected as the primary data used for fitting of the representative empirical equations. Though the temperature scale corrections are of the order of the data experimental uncertainties, all the temperatures given in ITS-48 and IPTS-68 have been converted to ITS-90. To convert solution compositions expressed in mass fraction w of the salt in the solution and in molality m to molar fraction x:

$$x = \frac{w/M_{\text{salt}}}{w/M_{\text{salt}} + (1 - w)/M_{H_2O}}$$

$$x = \frac{m}{m + 1/M_{H_2O}}$$

the following values of molar masses were used: 0.110 984 $\text{kg}\cdot\text{mol}^{-1}$ for $CaCl_2$[17] and 0.018 015 268 $\text{kg}\cdot\text{mol}^{-1}$ for water.[18]

Not all of the original works provide sufficient comparable evidence on which to base a judgment of the relative merits of the various sets of results. To assess the quality of the particular sets of experimental data, we used an objective quantitative procedure described elsewhere.[1] The experimental data were divided into two categories: primary data employed in the development of the correlation and secondary data used only for comparison purposes. The sources of the assessed sets of experimental data on the $T-x$ relation are listed in Table 3 and for the $p-T$ relation in Table 4. In the tables, the number of points used for fitting is given for the primary data sets while for the secondary data it equaled zero.

Only original unsmoothed experimental data were included in the data used for fitting of the empirical equations. That is why the data compilations by Seidel and Linke[75] and Garvin et al.[16] are not included here as separate sources of experimental data. The usable experimental data on the $T-x$ and $p-T$ solid−liquid equilibrium relations are available up to the molar fraction $x = 0.36$ (i.e., $T = 559$ K) and up to the molar fraction $x = 0.335$ (i.e., $T = 478$ K), respectively, both corresponding to the one-third hydrate.

Methodology

Description of the T−x Relation. It is the usual way to determine the coordinates of the two-solid saturation point from the intersection of the fits of the adjoining solubility curves.[11,76] This procedure, though simple and plausible, brings some difficulties. With a limited number of widely scattered data points, the resultant intersection of the fitting curves can in some cases substantially depend on the choice of independent variable, i.e. whether the $T-x$ data are fitted as a $T(x)$ or an $x(T)$ function

Table 1. Literature Data on the Temperature t and the Saturated Solution Mass Fraction w at Two-Solid Saturation Points of the $CaCl_2-H_2O$ System

solid phases		Guthrie[2]	Roozeboom[3]	Rodebush[4]	ICT[14]	Yanatieva[5]	Druzhinin and Shepelev[6]	Clynne and Potter[7]	Broul et al.[15]	Codata tables[16]	Conde[11]	this work
eutectic point	t/°C	−27.5	−55	−51		−49.8				−49.7	−54.23	−50.49
ice + $CaCl_2 \cdot 6H_2O$	100w	28	29.8	48		30.22				30.50	29.85	30.47
peritectic point	t/°C		29.8		30.0		30		30.1	29.7	28.93	29.65
$CaCl_2 \cdot 6H_2O$ + α-$CaCl_2 \cdot 4H_2O$	100w		50.1		50.66		49.72		49.38	49.2	49.84	49.55
peritectic point	t/°C		29.2		29.2					29.6	26.41	29.38
$CaCl_2 \cdot 6H_2O$ + β-$CaCl_2 \cdot 4H_2O$	100w		53.0		53.22					52.3	52.38	52.25
peritectic point	t/°C									29.4		28.78
$CaCl_2 \cdot 6H_2O$ + γ-$CaCl_2 \cdot 4H_2O$	100w									52.6		52.92
peritectic point	t/°C		45.3				45	45.19	45.1	45.4	44.98	45.25
α-$CaCl_2 \cdot 4H_2O$ + $CaCl_2 \cdot 2H_2O$	100w		56.6				55.92	55.73	55.93	56.15	56.63	56.09
peritectic point	t/°C				38.4		41		41.0	41.2	37.76	41.07
β-$CaCl_2 \cdot 4H_2O$ + $CaCl_2 \cdot 2H_2O$	100w				56.07		55.81		56.14	55.94	56.09	55.90
peritectic point	t/°C						39		38.5	39.0		37.85
γ-$CaCl_2 \cdot 4H_2O$ + $CaCl_2 \cdot 2H_2O$	100w						55.82		56.01	55.85		55.77
peritectic point	t/°C		175.5		175.5					175.85	176.33	176.4
$CaCl_2 \cdot 2H_2O$ + $CaCl_2 \cdot H_2O$	100w		74.8		74.8					72.91	74.86	73.01
peritectic point	t/°C									186.85		186.9
$CaCl_2 \cdot H_2O$ + $CaCl_2 \cdot {}^{f}/_{3}H_2O$	100w									74.7		74.71
peritectic point	t/°C									229.85		231.3
$CaCl_2 \cdot {}^{1}/_{3}H_2O$ + $CaCl_2$	100w									76.7		76.75

Table 2. Temperature T, Molar Fraction x, and Mass Fraction w of the Transition Points of the $CaCl_2-H_2O$ System with Estimates of Their Respective Standard Uncertainties u_T, u_x, and u_w

solid phases	$T \pm u_T$	$x \pm u_x$	t	$100w \pm u_w$
	K		°C	
ice + $CaCl_2 \cdot 6H_2O$	222.66 ± 0.80	0.06642 ± 0.0001	−50.49	30.47 ± 0.03
$CaCl_2 \cdot 6H_2O$ + α-$CaCl_2 \cdot 4H_2O$	302.80 ± 0.05	0.13751 ± 0.0003	29.65	49.55 ± 0.06
$CaCl_2 \cdot 6H_2O$ + β-$CaCl_2 \cdot 4H_2O$	302.53 ± 0.10	0.15082 ± 0.0003	29.38	52.25 ± 0.06
$CaCl_2 \cdot 6H_2O$ + γ-$CaCl_2 \cdot 4H_2O$	301.93 ± 0.15	0.15430 ± 0.0003	28.78	52.92 ± 0.06
α-$CaCl_2 \cdot 4H_2O$ + $CaCl_2 \cdot 2H_2O$	318.40 ± 0.30	0.17178 ± 0.0005	45.25	56.09 ± 0.09
β-$CaCl_2 \cdot 4H_2O$ + $CaCl_2 \cdot 2H_2O$	314.22 ± 0.90	0.17068 ± 0.0006	41.07	55.90 ± 0.10
γ-$CaCl_2 \cdot 4H_2O$ + $CaCl_2 \cdot 2H_2O$	311.00 ± 0.75	0.16990 ± 0.0016	37.85	55.77 ± 0.28
$CaCl_2 \cdot 2H_2O$ + $CaCl_2 \cdot H_2O$	449.55 ± 1.00	0.30509 ± 0.0010	176.4	73.01 ± 0.09
$CaCl_2 \cdot H_2O$ + $CaCl_2 \cdot {}^{1}/_{3}H_2O$	460.05 ± 1.00	0.32416 ± 0.0003	186.9	74.71 ± 0.03
$CaCl_2 \cdot {}^{1}/_{3}H_2O$ + $CaCl_2$	504.45 ± 5.00	0.34898 ± 0.0008	231.3	76.75 ± 0.06

as demonstrated by Pátek and Klomfar.[1] To avoid ambiguities, we used a procedure that treats both variables symmetrically. Data on temperature and composition are described using a parametric model

$$T(\tau) = T_L - (T_R - T_L)\tau + T_t \sum_{i=1}^{N} a_i \tau^{m_i} (1 - \tau)^{n_i} \tag{1}$$

$$x(\tau) = x_L - (x_R - x_L)\tau + \sum_{i=1}^{N} b_i \tau^{j_i} (1 - \tau)^{k_i} \tag{2}$$

where the value of the independent variable τ is defined as

$$\tau = \pm \frac{1}{\sqrt{2}} \left[\left(\frac{T - T_L}{T_R - T_L} \right)^2 + \left(\frac{x - x_L}{x_R - x_L} \right)^2 \right]^{1/2} \tag{3}$$

for any pair of values of temperature T and corresponding saturated solution composition x of an experimentally determined $T-x$ relation. To make the coefficient a_i dimensionless, the water triple point temperature $T_t = 273.16$ K was arbitrarily selected as the reference temperature value.

The polynomials 1 and 2 contain explicitly the temperatures T_L and T_R and compositions x_L and x_R of the transition points between hydrates. The subscripts L and R denote here the left and right end points of the interval, respectively. The negative values of the variable τ refer to the values of x less than x_L. The optimal coordinates of the transition points were found using a simultaneous minimizing of the mean square deviation of the least-squares fit of eqs 1 and 2 to the experimental data. For each given set of values of the transition point coordinates T_L, x_L, T_R, and x_R the coefficients a_i and b_i of the optimal fitting polynomials and the corresponding mean square deviation of the least-squares fit was computed. Those values of the parameters T_L, x_L, T_R, and x_R that minimize the mean square deviation were accepted as the best estimate of the coordinates of the transition points. In this way the method guarantees, that the resultant transition points will not depend on the choice of independent variable.

A stepwise least-squares regression technique by de Reuck and Armstrong[77] has been applied in the present work to determine the optimal set of polynomial terms to be incorporated into the fitting function. The procedure ensures statistical significance of the polynomial terms included and randomness of the deviations of the experimental data from values calculated from the resultant equation.

As soon as the approximation functions T(τ) and x(τ) are obtained, the dependence of T on x can be restored for any given composition x_0 by solving numerically the equation

$$x(\tau_0) = x_0 \tag{4}$$

to obtain the corresponding value τ_0 of the parameter τ. Then

Table 3. Sources of Data on the $T-x$ Relation of the $CaCl_2-H_2O$ System at Solid–Liquid Equilibrium

		range of values			
author(s)	year	temperature T/K	mass fraction $100w$	number of data total/used	solid phase[a]
Rüdorff[19]	1861	263 to 273	1 to 15	8/7	a
Mulder[20]	1866	273 to 372	33 to 61	14/0	b, c, f
Guthrie[2]	1876	236 to 273	1 to 39	12/0	a, b
Hammerl[21]	1879	223 to 303	30 to 51	23/17	b
Ditte[22]	1881	288	41.2	1/1	b
Arrhenius[23]	1888	271 to 273	0.5 to 3.5	4/4	a
Engel[24]	1888	273	27.3	1/1	b
Roozeboom[3]	1889	218 to 508	9 to 77	32/17	b, c, e, f, h, i
Pickering[25]	1892	271 to 273	0.001 to 3.412	27/27	a
Pickering[26]	1893	224 to 309	0.5 to 53	103/98	a, b, c
Étard[27]	1894	251 to 388	31 to 58	14/0	b, f
Pickering[28]	1894	225 to 302	4 to 53	50/50	a, b
Loomis[29]	1897	270 to 273	0.1 to 5.2	6/6	a
Jones and Getman[30]	1902	262 to 270	5 to 14	9/3	a
Lidbury[31]	1902	302.46 to 302.95	48.9 to 52.6	19/19	b
Jones and Getman[32]	1904	227 to 273	1 to 26	16/8	a
Johnston[33]	1907	220 to 273	0.5 to 34	7/4	a
Jones and Pearce[34]	1907	267 to 273	0.1 to 10	9/9	a
Jones and Stine[35]	1908	224 to 272	2 to 28	25/12	a
Weimarn[36]	1911	293 to 298	42 to 53	2/1	b
Milikan[37]	1917	318 to 323	56 to 57	2/0	c, f
Milikan[38]	1918	298	44.8	1/1	b
Rodebush[4]	1918	222 to 269	8 to 32	6/3	a
Klein and Svanberg[39]	1920	270.5 to 272.7	0.5 to 2.7	3/0	a
Pelling and Robertson[40]	1923	323 to 367	57 to 61	2/0	f
O'Connor[41]	1927	273	37.6	1/1	b
Mazzetti[42]	1929	293	42.7	1/1	b
de Carli[43]	1932	284 to 298	39 to 46	2/1	b
Ehret[44]	1932	298	45	1/1	b
Prutton and Tower[45]	1932	243 to 273	12 to 37	6/5	a, b
Bassett et al.[13]	1933	320 to 327	21 to 37	12/11	c, d, e
Bury and Davies[46]	1933	298	49	1/1	c
Igelsrud and Thompson[47]	1936	273	37.5	3/3	b
Tschischikoff and Schachoff[48]	1936	298 to 333	52 to 58	2/0	b, f
Bassett et al.[49]	1937	273 to 323	37 to 57	3/2	b, f
Kurnakov and Nikolaev[50]	1938	298	45	2/2	b
Yanatieva[5]	1946	223 to 295	16 to 43	15/15	a, b
Lightfoot and Prutton[51]	1946	308	51.3	1/1	c
Lightfoot and Prutton[52]	1947	348	58.6	1/0	f
Assarsson[53]	1950	323 to 368	56 to 60	3/0	f
Assarsson[54]	1950	291 to 368	42 to 60	3/1	b, f
Assarsson[55]	1950	383	62	1/0	f
Druzhinin and Shepelev[6]	1950	273 to 323	37 to 56	9/9	b, c, d, e, f
Makarov and Vol'nov[56]	1951	328 to 348	57 to 59	2/0	f
Blidin[57]	1952	298	46	1/1	b
Assarsson and Balder[58]	1953	291 to 373	42 to 61	8/6	b, c, f
Blidin[59]	1954	298 to 313	46 to 56	2/1	b, c
Makarov and Vol'nov[60]	1954	278 to 348	38 to 59	8/4	b, c, f
Mun and Darer[61]	1956	252 to 270	7 to 21	4/4	a
Shevtchuk and Vaisfel'd[62]	1967	298	44.8	1/1	b
Gibbard and Fong[63]	1975	269 to 273	0.6 to 13.9	10/0	a
Filippov and Mikhelson[64]	1977	298 to 308	44.5 to 51.1	2/2	b, c
Potter and Clynne[65]	1978	282 to 371	39 to 60	14/14	b, c, f
Clynne and Potter[7]	1979	322 to 433	56 to 68	9/9	f
Ketsko et al.[66]	1984	523 to 673	79 to 95	8/0	i
Sinke et al.[12]	1985	329 to 559	57 to 78	19/18	f, h, i
Pitzer and Shi[67]	1993	303 to 373	49 to 60	9/9	b, c, f
Masoudi et al.[68]	2005	273 to 333	33 to 58	9/5	b, c, f

[a] a, ice; b, hexahydrate; c, tetrahydrate alpha; d, tetrahydrate beta; e, tetrahydrate gamma; f, dihydrate; g, monohydrate; h, $^{1}/_{3}$ hydrate; i, anhydrous salt.

$T_0 = \mathrm{T}(\tau_0)$. Similarly, dependence of x on T can be obtained, representing the same $T-x$ relation as given by eqs 1 and 2 in a parametric form.

To start the optimizing procedure, the two-solid point coordinates were employed obtained from intersections of simple polynomials fitted to the experimental data. Of course, the obtained final results are self-consistent, i.e. when used as the starting values in the optimization of the two-solid point coordinates, the same values are reproduced by the procedure.

Table 4. Sources of Data on the $p-T$ Relation of the $CaCl_2-H_2O$ System at Solid−Liquid Equilibrium

author(s)	year	temperature T/K	number of data total/used	solid phase[a]
Roozeboom[3]	1889	218 to 478	51/47	a, c, f, g, h
Lescoeur[69]	1890	283 to 373	8/6	b, c, f
Baker and Waite[70]	1921	373 to 447	12/10	f
Ebert[71]	1930	273 to 293	4/4	b
Collins and Menzies[72]	1936	298 to 398	16/14	b, c, f
Lannung[73]	1936	312 to 318	25/25	b, c, d, e, f
Acheson and Wildhack[74]	1965	288 to 328	23/22	b, c, f

[a] a, ice; b, hexahydrate; c, tetrahydrate alpha, d, tetrahydrate beta; e, tetrahydrate gamma; f, dihydrate; g, monohydrate; h, $^{1}/_{3}$ hydrate.

Table 5. Coefficients and Exponents of Equation 8 for the $CaCl_2-H_2O$ System

	anhydrous salt			$CaCl_2\cdot6H_2O$			$CaCl_2\cdot2H_2O$		
	$T_L = 504.50$ K, $T_R = 755.00$ K $x_L = 0.34898$, $x_R = 1.00000$			$T_L = 222.66$ K, $T_R = 301.93$ K $x_L = 0.06642$, $x_R = 0.15430$			$T_L = 318.40$ K, $T_R = 449.53$ K $x_L = 0.17178$, $x_R = 0.30509$		
i	a_i	m_i	n_i	a_i	m_i	n_i	a_i	m_i	n_i
1	$5.37020\cdot10^{1}$	1	3	$4.94804\cdot10^{1}$	1	1	$1.51659\cdot10^{2}$	2	1
2	$1.62666\cdot10^{4}$	2	6	$-4.39227\cdot10^{3}$	4	1	$2.90106\cdot10^{2}$	1	2
3	$5.39021\cdot10^{2}$	7	2	$4.36863\cdot10^{7}$	3	4	$3.94269\cdot10^{7}$	1	8
4	$-4.63247\cdot10^{4}$	3	6	$1.32715\cdot10^{9}$	2	6			
5	$-4.38312\cdot10^{4}$	2	8	$-3.46615\cdot10^{11}$	3	7			
6	$7.96094\cdot10^{1}$	10	1						
7	$4.33075\cdot10^{4}$	5	6						
	α-$CaCl_2\cdot4H_2O$			β-$CaCl_2\cdot4H_2O$			γ-$CaCl_2\cdot4H_2O$		
	$T_L = 302.80$ K, $T_R = 318.40$ K $x_L = 0.13751$, $x_R = 0.17178$			$T_L = 302.53$ K, $T_R = 314.22$ K $x_L = 0.15082$, $x_R = 0.17068$			$T_L = 301.93$ K, $T_R = 311.00$ K $x_L = 0.15430$, $x_R = 0.16990$		
i	a_i	m_i	n_i	a_i	m_i	n_i	a_i	m_i	n_i
1	$3.53243\cdot10^{1}$	1	1	$2.19245\cdot10^{1}$	1	1	$4.39601\cdot10^{1}$	1	1
2	$6.23278\cdot10^{3}$	1	3	$-3.44196\cdot10^{2}$	2	1			
3	$-9.08750\cdot10^{5}$	3	2						
	ice			$CaCl_2\cdot H_2O$			$CaCl_2\cdot{}^{1}/_{3}H_2O$		
	$T_L = 273.16$ K, $T_R = 222.66$ K, $x_L = 0.00000$, $x_R = 0.06642$			$T_L = 449.53$ K, $T_R = 460.11$ K $x_L = 0.30509$, $x_R = 0.32416$			$T_L = 460.11$ K, $T_R = 504.50$ K $x_L = 0.32416$, $x_R = 0.34898$		
i	a_i	m_i	n_i						
1	$4.59475\cdot10^{1}$	1	1						
2	$-2.83999\cdot10^{2}$	1	2						
3	$3.18230\cdot10^{5}$	5	1						

Table 6. Coefficients and Exponents of Equation 9 for the $CaCl_2-H_2O$ System

	$CaCl_2\cdot6H_2O$			$CaCl_2\cdot2H_2O$		
	$p_L = 2.590\cdot10^{0}$ Pa, $p_R = 6.997\cdot10^{2}$ Pa $x_L = 0.06642$, $x_R = 0.15430$			$p_L = 1.587\cdot10^{3}$ Pa, $p_R = 1.133\cdot10^{5}$ Pa $x_L = 0.17178$, $x_R = 0.30509$		
i	b_i	m_i	n_i	b_i	m_i	n_i
1	$4.35016\cdot10^{6}$	1	1	$-3.60284\cdot10^{5}$	1	1
2	$-7.76531\cdot10^{7}$	1	2	$4.41401\cdot10^{6}$	1	2
3	$-6.95685\cdot10^{8}$	3	1	$2.31687\cdot10^{7}$	3	1
4	$4.10461\cdot10^{9}$	1	4	$-1.03222\cdot10^{9}$	2	4
5	$1.86308\cdot10^{10}$	5	1	$-7.18321\cdot10^{8}$	1	5
6	$-5.91665\cdot10^{10}$	1	6	$-9.11916\cdot10^{9}$	7	1
7	$-1.90561\cdot10^{11}$	7	1	$-1.29526\cdot10^{10}$	6	2
	ice			α-$CaCl_2\cdot4H_2O$		
	$p_L = 6.117\cdot10^{2}$ Pa, $p_R = 2.590\cdot10^{0}$ Pa $x_L = 0.00000$, $x_R = 0.06642$			$p_L = 9.011\cdot10^{2}$ Pa, $p_R = 1.587\cdot10^{3}$ Pa $x_L = 0.13751$, $x_R = 0.17178$		
i	b_i	m_i	n_i	b_i	m_i	n_i
1	$8.01638\cdot10^{4}$	2	1	$-1.71828\cdot10^{3}$	1	1
2	$-1.44981\cdot10^{9}$	4	2	$1.11871\cdot10^{5}$	1	2
3	$-4.75856\cdot10^{7}$	3	3	$1.86573\cdot10^{6}$	3	1
4	$1.30428\cdot10^{13}$	6	3	$-3.49489\cdot10^{7}$	1	4
5	$3.04224\cdot10^{12}$	1	9			
	β-$CaCl_2\cdot4H_2O$			γ-$CaCl_2\cdot4H_2O$		
	$p_L = 7.790\cdot10^{2}$ Pa, $p_R = 1.270\cdot10^{3}$ Pa $x_L = 0.15082$, $x_R = 0.17068$			$p_L = 7.080\cdot10^{2}$ Pa, $p_R = 1.069\cdot10^{3}$ Pa $x_L = 0.15430$, $x_R = 0.16990$		
i	b_i	m_i	n_i	b_i	m_i	n_i
1	$4.98020\cdot10^{2}$	1	1	$6.21443\cdot10^{2}$	1	1
2	$-7.72002\cdot10^{3}$	2	1	$-3.14938\cdot10^{4}$	2	1
	$CaCl_2\cdot H_2O$			$CaCl_2\cdot{}^{1}/_{3}H_2O$		
	$p_L = 1.133\cdot10^{5}$ Pa $p_R = 1.396\cdot10^{5}$ Pa $x_L = 0.30509$ $x_R = 0.32416$			$p_L = 1.396\cdot10^{5}$ Pa $p_R = 3.313\cdot10^{5}$ Pa $x_L = 0.32416$ $x_R = 0.34898$		

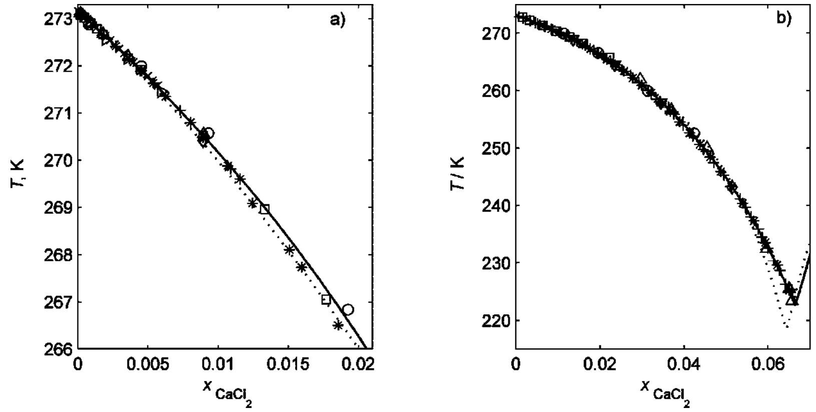

Figure 3. Water−ice branch of the SLE phase diagram for the $CaCl_2-H_2O$ system; temperature T as a function of the salt mole fraction x_{CaCl_2}. Primary data: (a) open right-pointing triangle, Arrhenius;[23] ×, Pickering;[25] Δ, Loomis;[29] ◇, Jones and Getman;[30] +, Jones and Getman;[32] ○, Johnston;[33] □, Jones and Pearce;[34] ∗, Jones and Stine;[35] (b) □, Rüdorff;[19] +, Pickering;[26] ∗, Pickering;[28] ▽, Rodebush;[4] ◇, Prutton and Tower;[45] Δ, Yanatieva;[5] ○, Mun and Darer.[61] •••••, Conde;[11] —, this work.

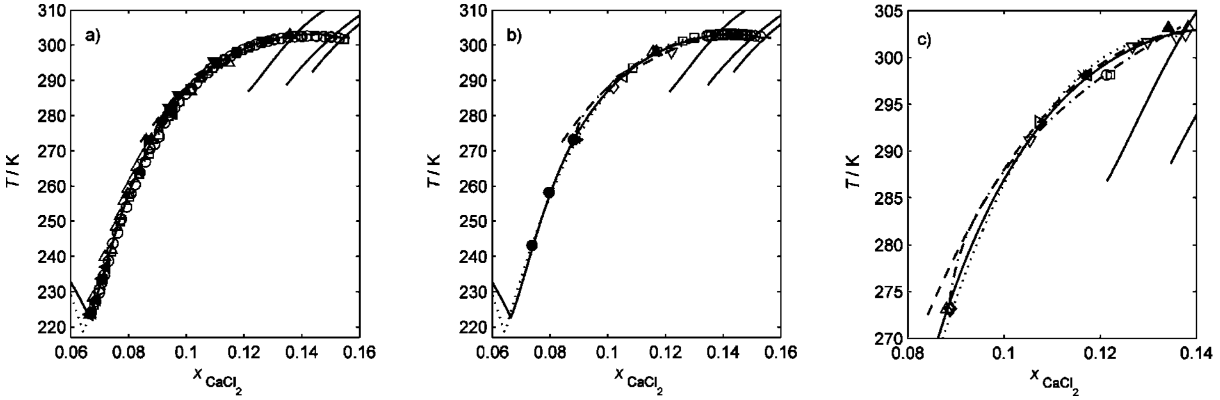

Figure 4. Hexahydrate branch of the SLE phase diagram for the $CaCl_2-H_2O$ system; temperature T as a function of the salt mole fraction x_{CaCl_2}. Primary data: (a) △, Hammerl;[21] ○, Pickering;[26] □, Pickering;[28] ■, Bassett et al.;[49] filled left-pointing triangle, Yanatieva;[5] ◆, Makarov and Vol'nov;[60] ▼, Potter and Clynne;[65] ▲, Pitzer and Shi;[67] (b) ◇, Ditte;[22] ∗, Engel;[24] □, Roozeboom;[3] ○, Lidbury;[31] open right-pointing triangle, O'Connor;[41] ▲ Ehret;[44] ●, Prutton and Tower;[45] open left-pointing triangle, Assarsson;[54] ▽, Blidin;[57] △, Filippov and Mikhelson;[64] (c) open right-pointing triangle, Weimarn;[36] ×, Milikan;[38] ∗, Mazzetti;[42] ○, de Carli;[43] ◇, Igelsrud and Thompson;[47] open left-pointing triangle, Kurnakov and Nikolaev;[50] △, Druzhinin and Shepelev;[6] ▽, Assarsson and Balder;[58] □, Blidin;[59] +, Shevtchuk and Vaisfel'd;[62] ▲, Masoudi et al.[68] —•—•—, Broul et al.;[15] •••••, Conde;[11] −−−−, Zeng et al.;[10] —, this work.

Inclusion of the p−T Relation into the Optimization Procedure. On the basis of eqs 1 and 2, the experimental data on the $p-T$ relation of the dependence of the saturated solution vapor pressure on temperature can be transformed to the $p-x$ form. The $p-x$ relation can be described within a parametric model quite analogous to that given by eqs 1 and 2:

$$\ln[p(\tau)] = \ln(p_L) - [\ln(p_R) - \ln(p_L)]\tau + \sum_{i=1}^{N} c_i \tau^{m_i}(1-\tau)^{n_i} \qquad (5)$$

$$x(\tau) = x_L - (x_R - x_L)\tau + \sum_{i=1}^{N} d_i \tau^{j_i}(1-\tau)^{k_i} \qquad (6)$$

where the value of the independent variable τ is defined as

$$\tau = \pm\frac{1}{\sqrt{2}}\left[\left(\frac{\ln(p)-\ln(p_L)}{\ln(p_R)-\ln(p_L)}\right)^2 + \left(\frac{x-x_L}{x_R-x_L}\right)^2\right]^{1/2} \qquad (7)$$

In this way experimental data on the $p-T$ relation have been used to find transition compositions simultaneously with the $T-x$ data.

The approach used represents a powerful tool for data approximation and interpolation in cases when few data are available or when the data are widely scattered. Most often one

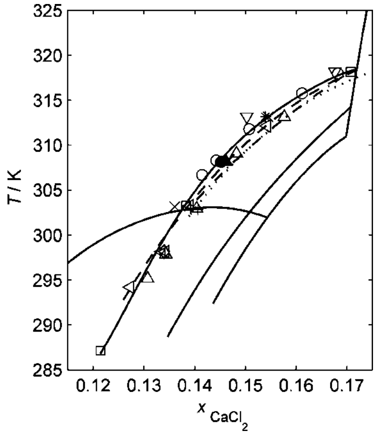

Figure 5. α-Tetrahydrate branch of the SLE phase diagram for the $CaCl_2-H_2O$ system; temperature T as a function of the salt mole fraction x_{CaCl_2}. Primary data: △, Roozeboom;[3] open left-pointing triangle, Bassett et al.;[13] ◇, Bury and Davies;[46] ▲, Lightfoot and Prutton;[51] □, Druzhinin and Shepelev;[6] +, Assarsson and Balder;[58] ×, Makarov and Vol'nov;[60] ●, Filippov and Mikhelson;[64] ○, Potter and Clynne;[65] ∗, Pitzer and Shi;[67] ▽, Masoudi et al.[68] —•—•—, Broul et al.;[15] •••••, Conde;[11] −−−−, Zeng et al.;[10] —, this work.

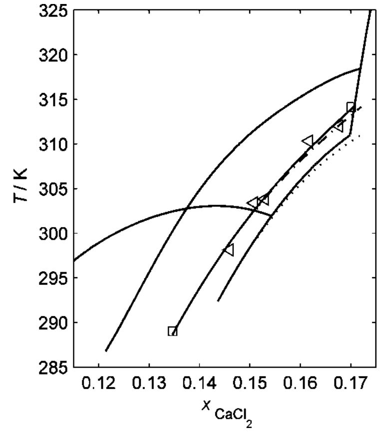

Figure 6. β-Tetrahydrate branch of the SLE phase diagram for the $CaCl_2-H_2O$ system; temperature T as a function of the salt mole fraction x_{CaCl_2}. Primary data: open left-pointing triangle, Bassett et al.;[13] □, Druzhinin and Shepelev.[6] —•—•—, Broul et al.;[15] •••••, Conde;[11] —, this work.

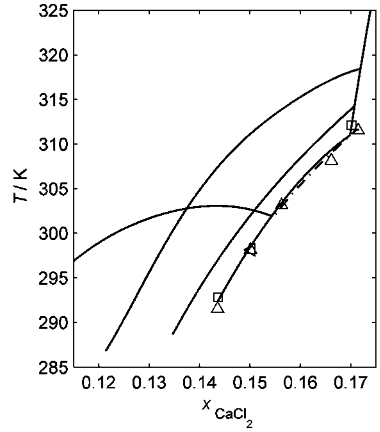

Figure 7. γ-Tetrahydrate branch of the SLE phase diagram for the $CaCl_2-H_2O$ system; temperature T as a function of the salt mole fraction x_{CaCl_2}. Primary data: △, Roozeboom;[3] open left-pointing triangle, Bassett et al.;[13] □, Druzhinin and Shepelev.[6] —•—•—, Broul et al.;[15] —, this work.

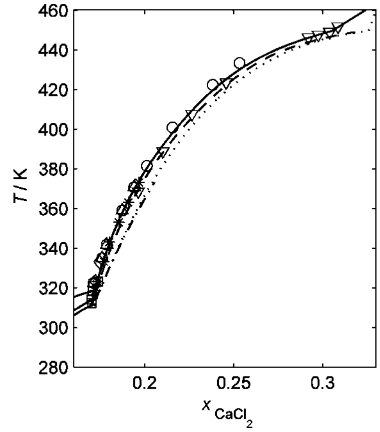

Figure 8. Dihydrate branch of the SLE phase diagram for the $CaCl_2-H_2O$ system; temperature T as a function of the salt mole fraction x_{CaCl_2}. Primary data: □, Druzhinin and Shepelev;[6] △, Potter and Clynne;[65] ○, Clynne and Potter;[7] ▽, Sinke et al.;[12] ∗, Pitzer and Shi.[67] —•—•—, Broul et al.;[15] •••••, Conde;[11] ————, Zeng et al.;[10] —, this work.

or two and at the most four members in polynomials 1 and 2 are sufficient for approximation. The used transformation of the $p-T$ relation into the $p-x$ one makes it possible to approximate the saturated solution vapor pressure for hexahydrate, which is not a single-valued function of the variable T.

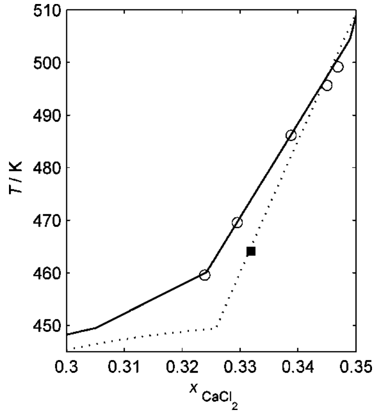

Figure 9. Monohydrate and one-third hydrate branches of the SLE phase diagram for the $CaCl_2-H_2O$ system; temperature T as a function of the salt mole fraction x_{CaCl_2}. Primary data: ○, Sinke et al.[12] Rejected data: ■, Roozeboom.[3] •••••, Conde;[11] —, this work.

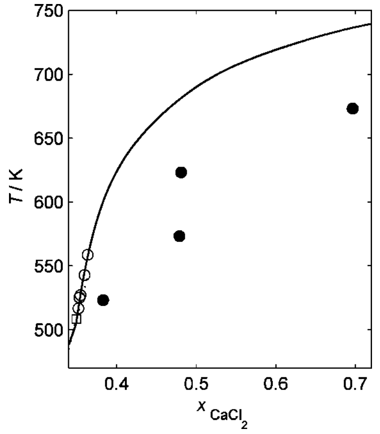

Figure 10. Anhydrate branch of the SLE phase diagram for the $CaCl_2-H_2O$ system; temperature T as a function of the salt mole fraction x_{CaCl_2}. Primary data: □, Roozeboom;[3] ○, Sinke et al.[12] Rejected data: ●, Ketsko et al.[66] •••••, Conde;[11] —, this work.

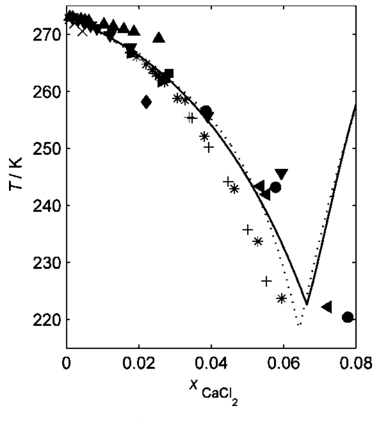

Figure 11. Water−ice branch of the SLE phase diagram for the $CaCl_2-H_2O$ system; temperature T as a function of the salt mole fraction x_{CaCl_2}. Rejected data: ■, Rüdorff;[19] ▼, Guthrie;[2] filled right-pointing triangle, Jones and Getman;[30] +, Jones and Getman;[32] ●, Johnston;[33] ∗, Jones and Stine;[35] filled left-pointing triangle, Rodebush;[4] ×, Klein and Svanberg;[39] ◆, Prutton and Tower;[45] ▲, Gibbard and Fong.[63] •••••, Conde;[11] —, this work.

The inclusion of the $p-T$ relation provides an additional criterion of data accuracy. Similarly, as the experimental data on $T-x$ relation give T- and x-coordinates of the transition points by the intersection points of adjacent hydrate branches of the solubility curve, experimental data on $p-T$ relation imply certain pressure and temperature coordinates of the same transition points. Therefore, accurate $T-x$ and $p-T$ data should show equal

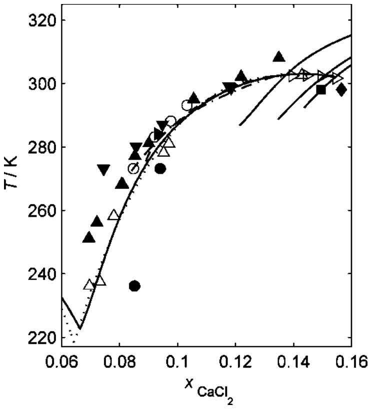

Figure 12. Hexahydrate branch of the SLE phase diagram for the $CaCl_2-H_2O$ system; temperature T as a function of the salt mole fraction x_{CaCl2}. Rejected data: ▼, Mulder;[20] •, Guthrie;[2] △, Hammerl;[21] ▲, Étard;[27] right-pointing triangle, Pickering;[28] ◇, Weimarn;[36] left-pointing triangle, de Carli;[43] ■, Tschischikoff and Schachoff;[48] ○, Masoudi et al.[68] —•—•—, Broul et al.;[15] •••••, Conde;[11] ————, Zeng et al.;[10] —, this work.

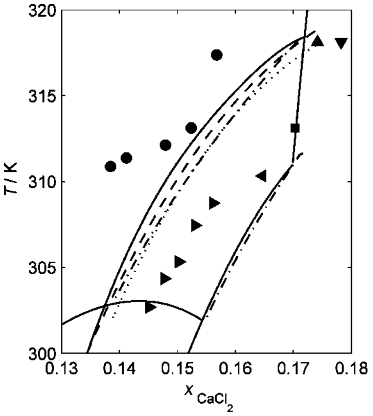

Figure 13. α-Tetrahydrate and γ-tetrahydrate branches of the SLE phase diagram for the $CaCl_2-H_2O$ system; temperature T as a function of the salt mole fraction x_{CaCl_2}. Rejected data: ●, Mulder;[20] ▲, Roozeboom;[3] right-pointing triangle, Pickering;[26] ▼, Milikan;[37] left-pointing triangle, Bassett et al.;[13] ■, Blidin.[59] —•—•—, Broul et al.;[15] •••••, Conde;[11] ————, Zeng et al.;[10] —, this work.

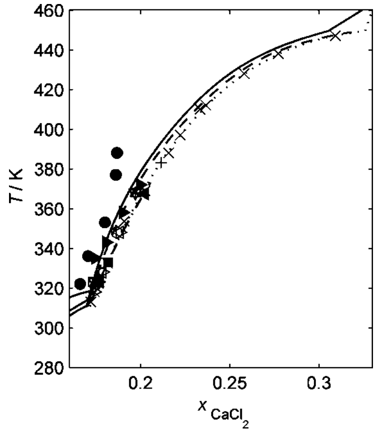

Figure 14. Dihydrate branch of the SLE phase diagram for the $CaCl_2-H_2O$ system; temperature T as a function of the salt mole fraction x_{CaCl_2}. Rejected data: filled right-pointing triangle, Mulder;[20] ×, Roozeboom;[3] ●, Étard;[27] ◇, Milikan;[37] filled left-pointing triangle, Pelling and Robertson;[40] ■, Tschischikoff and Schachoff;[48] △, Bassett et al.;[49] ○, Lightfoot and Prutton;[52] ▽, Assarsson;[53] □, Assarsson;[54] +, Assarsson;[55] open left-pointing triangle, Makarov and Vol'nov;[56] ∗, Assarsson and Balder;[58] open right-pointing triangle, Makarov and Vol'nov.[60] —•—•—, Broul et al.;[15] •••••, Conde;[11] ————, Zeng et al.;[10] —, this work.

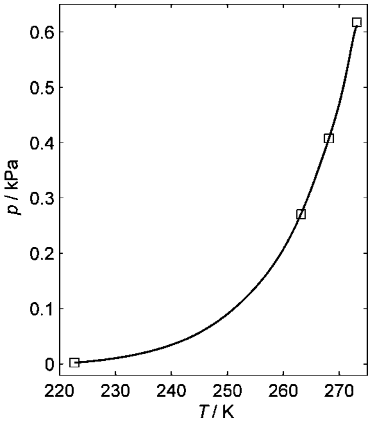

Figure 15. Water−ice branch of the SLE phase diagram for the $CaCl_2-H_2O$ system; pressure p as a function of temperature T. Primary data: □, Roozeboom.[3] —, this work.

temperature coordinates of the transition point. And furthermore, after conversion of the $p-T$ relation to its $p-x$ form, the $T-x$ and $p-x$ data should show equal x-coordinates of the transition point. Of course, in practice, precise equality is not attained. Consistent $T-x$ and $p-T$ data have their transition temperatures close one to another, where the closeness of the temperatures should be measured by their standard uncertainties estimated from the data scatter.

The existence of the three tetrahydrate modifications introduces some additional difficulty into the optimization procedure. From the six transition temperatures of the three modifications of the tetrahydrate, only two transition temperatures are independent so that they can be included among the optimized parameters. The transition temperature T_L of an arbitrary one of the three left end points and the transition temperature T_R of an arbitrary one of the three right end points can be selected for optimization. The transition temperatures of the remaining four transition points of the tetrahydrate modifications are then determined by the intersection of their solubility curves with the solubility curve of the neighboring hexahydrate or dihydrate at their common transition composition. The same is valid for saturated solution vapor pressures at the transition points of the tetrahydrate modifications. The lowered number of the free parameters results thus in a strong constraint on the coordinates of the transition points that should be fulfilled throughout the whole optimization procedure.

In the light of this constraint, only some data on the $T-x$ relation proved to be compatible with the $p-T$ data while the other should have been rejected.

It is somewhat cumbersome to use the resultant parametric eqs 1 and 2 as well as 5 and 6 in practical calculations. That is why we present here explicit functions $T(x)$ and $p(x)$ obtained as an approximation of the data generated from the above parametric form of the relations $T-x$ and $p-x$:

$$T(x) = T_L + \frac{T_R - T_L}{x_R - x_L}(x - x_L) + T_t \sum_{i=1}^{N} a_i (x - x_L)^{m_i} (x_R - x)^{n_i} \qquad (8)$$

$$\ln[p(x)] = \ln(p_L) + \frac{\ln(p_R) - \ln(p_L)}{x_R - x_L}(x - x_L) + \sum_{i=1}^{N} b_i (x - x_L)^{m_i} (x_R - x)^{n_i} \qquad (9)$$

To makethe coefficient a_i dimensionless, the water triple point temperature T_t = 273.16 K was arbitrarily selected as the reference temperature value.

Table 7. $CaCl_2-H_2O$ System[a]

solid phases	RMSD/K	100·RRMS
ice	0.18	0.07
$CaCl_2\cdot6H_2O$	0.93	0.36
α-$CaCl_2\cdot4H_2O$	1.2	0.39
β-$CaCl_2\cdot4H_2O$	0.60	0.21
γ-$CaCl_2\cdot4H_2O$	0.70	0.23
$CaCl_2\cdot2H_2O$	2.3	0.66
$CaCl_2\cdot H_2O$		
$CaCl_2\cdot{}^1/_3H_2O$	1.2	0.24
$CaCl_2$	1.5	0.25

[a] Absolute (RMSD) and relative (RRMS) root mean square deviations of the experimental $T-x$ data from eq 8.

Table 8. $CaCl_2-H_2O$ System[a]

solid phases	RMSD/Pa	100·RRMS
ice	3.1	0.52
$CaCl_2\cdot6H_2O$	12	3.2
α-$CaCl_2\cdot4H_2O$	21	2.0
β-$CaCl_2\cdot4H_2O$	10	1.2
γ-$CaCl_2\cdot4H_2O$	7.8	1.2
$CaCl_2\cdot2H_2O$	1500	3.5
$CaCl_2\cdot H_2O$		
$CaCl_2\cdot{}^1/_3H_2O$	545	0.32

[a] Absolute (RMSD) and relative (RRMS) root mean square deviations of the experimental $p-x$ data from eq 9.

Results

Table 1 gives the obtained $T-x$ coordinates of the transition points of the $CaCl_2-H_2O$ system. Table 5 shows the coefficients a_i and the exponents n_i and m_i of eq 8 describing the $T-x$ relation, while Table 6 gives the coefficients b_i and the exponents of eq 9 for the $p-x$ relation. In Figures 3 to 10, the $T-x$ experimental data points are depicted together with the solid−liquid equilibrium curves in the $T-x$ plane computed from the resultant representative eq 8.

Table 2 summarizes temperature and composition coordinates of the transition points together with estimates of their standard uncertainties with temperatures given both in kelvin and degrees Celsius and solution compositions in mass fraction and molar fraction. The optimization procedure used defines the coordinates of the transition points as functions of all data points (T, x) of the two hydrate crystallization curves adjacent to the transition point. Therefore, standard uncertainties of the transition point coordinates can be estimated by a straightforward application of the rule of propagation of uncertainties. As estimates of standard uncertainties of the data point compositions x and temperatures T their standard deviations from the representative equations were used.

The obtained description of the $T-x$ relation for the saturated solution in equilibrium with ice is based especially on the data of Rüdorff,[19] Arrhenius,[23] Pickering,[25,28] Loomis,[29] Jones and Pearce,[34] Yanatieva,[5] and Mun and Darer[61] which are highly consistent with each other (Figure 3). The rejected data by Guthrie,[2] Jones and Getman,[32] Jones and Stine,[35] Klein and Svanberg,[39] and Gibbard and Fong[63] show an evident systematic deviation from them (Figure 11).

As shown in Figure 4, the data generated by eq 8 for the hexahydrate agree well with the experimental data of Pickering,[26] Hammerl,[21] Lidbury,[31] Yanatieva,[5] and Assarsson and Balder.[58] The data by Etard,[27] Mulder,[20] and Masoudi et al.[68] were rejected as being systematically shifted (Figure 12). The four rejected data points by Pickering[28] deteriorated the mutual consistency of the $T-x$ and $p-T$ data in the sensitive region of coexistence of subcooled solution and hexahydrate.

The description of the solubility curve of α-$CaCl_2\cdot4H_2O$ is based especially on the data by Potter and Clynne,[65] Roozeboom,[3] and Bassett et al.[13] The rejected data by Mulder[20] show an excessive systematic deviation (Figure 13). In determination of the transition points of the tetrahydrate modifications, also metastable experimental points have been taken into account as depicted in Figures 5 and 17.

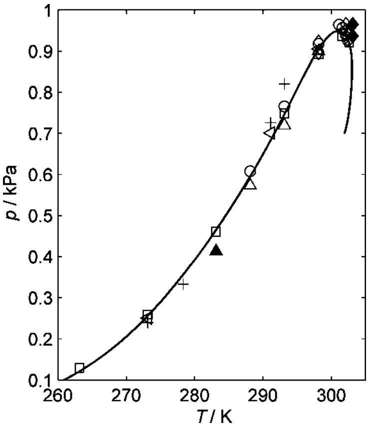

Figure 16. Hexahydrate branch of the SLE phase diagram for the $CaCl_2-H_2O$ system; pressure p as a function of temperature T. Primary data: △, Lescoeur;[69] +, Ebert;[71] ◇, Collins and Menzies;[72] open left-pointing triangle, Lannung;[73] ○, Acheson and Wildhack.[74] Rejected data: ▲, Lescoeur;[69] ◆, Collins and Menzies.[72] —, this work.

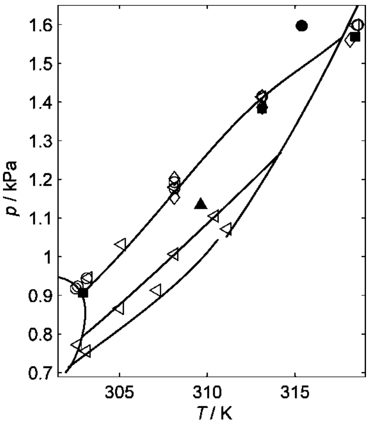

Figure 17. α, β, and γ-Tetrahydrate branches of the SLE phase diagram for the $CaCl_2-H_2O$ system; pressure p as a function of temperature T. Primary data: ◇, Collins and Menzies;[72] open left-pointing triangle, Lannung;[73] ○, Acheson and Wildhack.[74] Rejected data: ■, Roozeboom;[3] ▲, Lescoeur;[69] ●, Acheson and Wildhack.[74] —, this work.

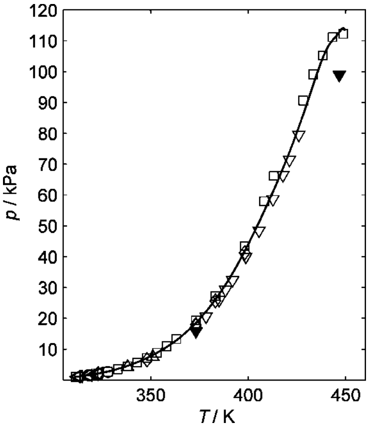

Figure 18. Dihydrate branch of the SLE phase diagram for the $CaCl_2-H_2O$ system; pressure p as a function of temperature T. Primary data: □, Roozeboom;[3] △, Lescoeur;[69] ▽, Baker and Waite;[70] ◇, Collins and Menzies;[72] open left-pointing triangle, Lannung;[73] ○, Acheson and Wildhack.[74] Rejected data: ▼, Baker and Waite.[70] —, this work.

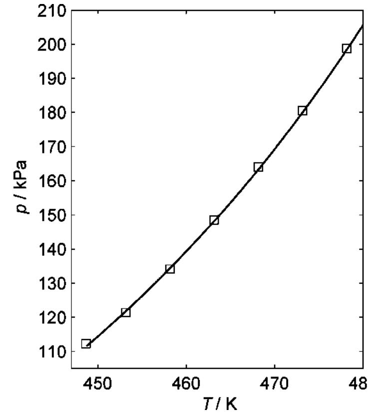

Figure 19. Monohydrate and one-third hydrate branches of the SLE phase diagram for the $CaCl_2-H_2O$ system; pressure p as a function of temperature T. Primary data: □, Roozeboom.[3] —, this work.

The data on the solid−liquid equilibrium phase diagram for $CaCl_2\cdot 2H_2O$ are the most conflicting. The data[3,27,53−56,58,60] (Figure 14) have proven not to be correlatable with the $p-x$ data using a common solution composition value at the transition points between the dihydrate and the three modifications of the tetrahydrate. Only the most recent data on $CaCl_2\cdot 2H_2O$ of Sinke et al.,[12] Clynne and Potter,[7] and also the data of Pitzer and Shi[67] and Druzhinin and Shepelev[6] (Figure 8) proved to be consistent with the transition compositions resulting from the $p-x$ relation.

Only the data by Sinke[12] are available for monohydrate and one-third hydrate. Nevertheless, the data show a clear difference in their slope for these two hydrates (Figure 9). The present description of the anhydride represents only interpolation of the data by Sinke and the fusion temperature for pure $CaCl_2$ (Figure 10).

In Figures 15 to 19, $p-T$ experimental data points are depicted together with the solid−liquid equilibrium curves in the $p-T$ plane obtained by combining the values computed from eqs 8 and 9. In the case of the γ-tetrahydrate and the dihydrate, the mutual inconsistency of the experimental data on the $T-x$ and $p-T$ relations made it impossible to find a p coordinate value for the transition point between them common to both hydrates (Figure 17).

Tables 7 and 8 give the absolute and relative root-mean-square deviations of the experimental data from eqs 8 and 9, respectively. The deviations give an idea of the scatter in the data around the fitted curves and through it an idea of the uncertainty of the temperature when calculated from the model. In general, the primary data on the $T-x$ relation show mean relative deviations almost by an order of magnitude smaller than the data on the $p-x$ relation.

Conclusion

Empirical equations describing the solid−liquid equilibrium $T-x$ and $p-x$ relations of the $CaCl_2-H_2O$ system have been developed based upon a body of critically assessed experimental data. Temperature, pressure, and saturated solution composition coordinates corresponding to the transition points between hydrates were derived from the data. To obtain unambiguous coordinates of the transition points a method based on a combined linear and nonlinear optimization procedure was used.

The relative uncertainties associated with the data correlation can be estimated (Tables 7 and 8) to range from ± 0.2 K for ice to ± 2.3 K for the dihydrate in the case of the $T-x$ relation. In the case of the $p-x$ relation, the uncertainties range from 0.5 % for ice to 3.5 % for the dihydrate.

Comparisons of the available measurements on the solid−liquid equilibrium of the $CaCl_2-H_2O$ system have shown that the amount of available experimental data is far less valuable to establish a description of that property of the systems than it might appear at a first glance. Some of the available sets of the solid−liquid equilibrium data are only of limited value, because they show large scatter or systematic deviations when compared to other data. The largest gap in the data on the $CaCl_2-H_2O$ system is clearly found in the region of compositions corresponding to saturated solution in equilibrium with the tetrahydrate modifications and with the monohydrate and one-third hydrate. The present results may be useful in planning new experiments.

List of Symbols

a_i	coefficients of the fitting polynomial
b_i	coefficients of the fitting polynomial
N	number of the fitting polynomial terms
M	molar mass, $kg\cdot mol^{-1}$
m	molality, $mol\cdot kg^{-1}$
m_i	exponents of the fitting polynomial
n_i	exponents of the fitting polynomial
p	pressure, Pa
RMSD	absolute root-mean-square deviation; RMSD = $[1/N\sum(z_{exp} - z_{cat})^2]^{1/2}$
RRMS	relative root-mean-square deviation; RRMS = $[1/N\sum(z_{exp}/z_{cat} - 1)^2]^{1/2}$
t	temperature, deg C
T	temperature, K
u	standard uncertainty
w	mass fraction of salt in the solution
x	molar fraction of salt in the solution

Subscripts

L	left end point of the hydrate interval
R	right end point of the hydrate interval
t	at triple point

Physical Constants

M_{CaCl_2}	$0.110984\ kg\cdot mol^{-1}$ [17]
M_{H_2O}	$0.018015268\ kg\cdot mol^{-1}$ [18]
T_t	273.16 K [18]

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