THEREDA Journal

Short Communication

Calcium Hydroxide Chlorides in THEREDA
-
Correction of phase stoichiometries

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Abstract: Calcium hydroxide chlorides are ternary compounds occurring in the basic system $Ca(OH)_2$ –$CaCl_2$ –H_2O as well as more complex systems. According to their composition $xCa(OH)_2 \cdot yCaCl_2 \cdot zH_2O$ they are also referred to as x-y-z-phases. Until 2019, literature was contradictory concerning their phase stoichiometries. Häusler et al. (Häusler, F., Schmidt, H., Freyer, D. *Journal of Inorganic and General Chemistry*, 645, (2019), pp. 723–731, DOI 10.1002/zaac.201900051.) precisely determined the compositions of the two existing phases as the hydrate $3Ca(OH)_2 \cdot CaCl_2 \cdot 12H_2O$ (3-1-12) and the anhydrous phase $Ca(OH)_2 \cdot CaCl_2$ (1-1-0).
Until now, the stoichiometries $3Ca(OH)_2 \cdot CaCl_2 \cdot 13H_2O$ (3-1-13) and $Ca(OH)_2 \cdot CaCl_2 \cdot H_2O$ (1-1-1) are implemented in THEREDA, according to the model of Harvie et al. (Harvie, C. E., Møller, N., Weare, J. H *Geochimica et Cosmochimica Acta*, 48, (1984), pp. 723–751, DOI 10.1016/0016-7037(84)90098-X.). With the correction of the two phase compositions in THEREDA, an adjustment of the solubility constants is necessary as described in the present Short communication.

The description of the $Ca(OH)_2$ – $CaCl_2$ – H_2O system within THEREDA is explained in detail in [ALT/BRE2011]. Numerical values for the Pitzer parameters and standard Gibbs energies of formation are listed in [VOI2020].

Besides the binary Portlandite ($Ca(OH)_2$) and calcium chloride hydrates ($CaCl_2 \cdot zH_2O$, z=2, 4, 6), calcium hydroxide chlorides may be found as ternary compounds in the system. According to their composition $xCa(OH)_2 \cdot yCaCl_2 \cdot zH_2O$ they are referred to as x-y-z-phases.

Within literature, a water rich phase 3-1-z with z = 8…13 and a second phase 1-1-z with z = 0…4 are described (cf. Table 1). Häusler et al. [HAU/SCH2019] were able to clarify these inconsistent phase stoichiometries by systematic solubility studies at 25, 40 and 60 °C and the application of Schreinemakers' method. The authors identified $3Ca(OH)_2 \cdot CaCl_2 \cdot 12H_2O$ (3-1-12) and the anhydrous phase $Ca(OH)_2 \cdot CaCl_2$ (1-1-0) as the thermodynamic stable phases.

Up to now, phase stoichiometries implemented in THEREDA have been the same as chosen by Harvie et al. [HAR/MOL1984] for their thermodynamic model (i.e. $3Ca(OH)_2 \cdot CaCl_2 \cdot 13H_2O$ and $Ca(OH)_2 \cdot CaCl_2 \cdot H_2O$).

The correction of phase compositions towards 3-1-12 and 1-1-0 phase has to go along with the readjustment of their solubility constants (standard Gibbs energies of formation, respectively) as described in the following.

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https://nbn-resolving.org/urn:nbn:de:bsz:105-qucosa2-967422

Table 1: Publications on solubility data for the system $Ca(OH)_2$ – $CaCl_2$ – H_2O.

Literature	Temperature investigated /K	stoichiometry reported for the $xCaCl_2 \cdot yCa(OH)_2 \cdot zH_2O$ (x-y-z) phases
[LUN/ZAH1892]	293, 313, 333, 353, 373	no information given
[SCH/FIG1911]	298	4-1-10, 1-1-0
[MIL1918]	283, 298, 313, 318, 321, 323	3-1-13, 1-1-1, 1-1-(3…4)
[OCO1927]**	273	3-1-13
[WRI/ASK1930]*	289…293	no information given
[HAY1934]*	373	no information given
[NIK/GLI1934]*	298	3-1-11
[REP/LEG1938]	323	$CaCl_2 \cdot CaO \cdot 5H_2O$, 1-1-1
[MAK/VOL1954]	278, 283, 303, 313	3-1-12, 1-1-1
[VOL/LAT1957]	253	3-1-12
[TRA/POP1961]**	323, 348, 353	1-1-1, 2-1-1
[MOZ/ZOZ1983]	303, 323, 373	3-1-12
[HAU/SCH2019]	298, 313, 333	3-1-12, 1-1-0

* values not included in data collection of this work (cf. text)
** values included in Figure 1 and Figure 2 but not into the fitting procedure (cf. text)

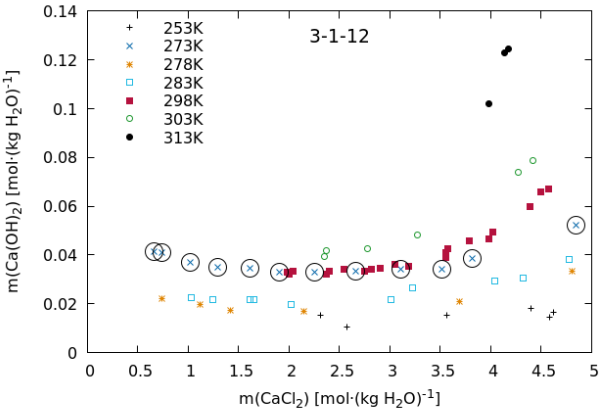

Figure 1: Solubility of the 3-1-12 phase, $3Ca(OH)_2 \cdot CaCl_2 \cdot 12H_2O$, according to literature data from Table A-1. Datapoints with reported phase stoichiometries of 3-1-13 or 3-1-11 are included. Circled datapoints: rejected data from [OCO1927].

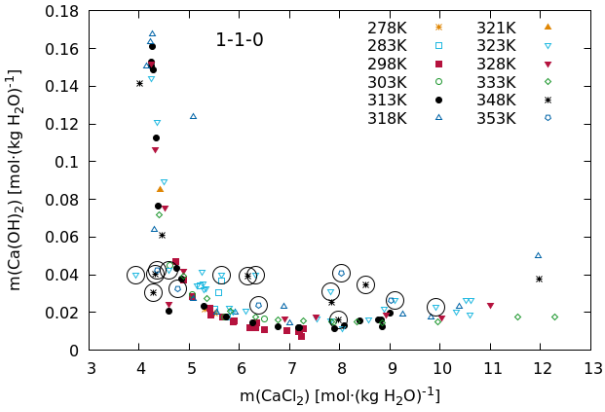

Figure 2: Solubility of the 1-1-0 phase, $Ca(OH)_2 \cdot CaCl_2$, according to literature data from Table A-1. Datapoints with reported phase stoichiometries of 1-1-1 are included. Circled datapoints: rejected data from [TRA/POP1961].

A collection of solubility data for the calcium hydroxide chloride phases was established from the literature listed in Table 1 (cf. Table A-1 in the appendix). Data from the following publications are not included: [WRI/ASK1930] (neither information on an exact investigation temperature nor analysis of solid phases); [HAY1934] (given solution composition could not be converted to mol/kg H_2O); [NIK/GLI1934] (difficulties in recalculating solution composition).

Figure 1 and Figure 2 show a graphical representation of solubilities assigned to the 3-1-12 and the 1-1-0 phase, respectively.

From Figure 1 it can be seen that the 273 K data from [OCO1927] correspond to other authors' 298 K data but do not follow the general

temperature trend. Hence, the author's declaration of his working temperature might be put into question. His data were therefore rejected from the fit.
Figure 2 shows a remarkable scattering in the data of [TRA/POP1961] (323, 348 and 353 K). As a result, these values were not included into the fitting procedure for the solubility constant of the 1-1-0 phase.

From solution compositions in equilibrium, solubility constants for the 3-1-12 and the 1-1-0 phase have been calculated according to equations (1) and (2), respectively.

$$K_{sp}(3\text{-}1\text{-}12) = a^4(Ca^{2+})\cdot a^2(Cl^-)\cdot a^6(OH^-)\cdot a^{12}(H_2O) = a^4(Ca^{2+})\cdot a^2(Cl^-)\cdot a^{12}(H_2O)\cdot a^{-6}(H^+) \quad (1)$$

$$K_{sp}(1\text{-}1\text{-}0) = a^2(Ca^{2+})\cdot a^2(Cl^-)\cdot a^2(OH^-) = a^4(Ca^{2+})\cdot a^2(Cl^-)\cdot a^2(H_2O)\cdot a^{-2}(H^+) \quad (2)$$

with

$$a(OH^-) = a(H_2O) \,/\, a(H^+) \quad (3)$$

The calculation of activities and solubility constants was performed with the PHREEQC program[1] and the Pitzer interaction parameter as stated in the 2020 release of THEREDA [VOI2020]. Resulting $\log_{10}K_{sp}$ values for the 3-1-12 and the 1-1-0 phase are tabulated in Table A-1 for each composition and temperature.

A temperature function of the general form (4) was then used to fit the isothermal data to (T = temperature in K).

$$\log_{10}K_{sp}(T) = A + B\cdot T + C\cdot T^2 + D/T + E/T^2 + F\cdot \ln T \quad (4)$$

All datapoints were included into the fit with a weight of 1. Figure 3 and Figure 4 show the quality of the fitted functions for the solubility constants for the 3-1-12 and the 1-1-0 phase, respectively.

[1] PHREEQC Version 3 (https://www.usgs.gov/software/phreeqc-version-3)

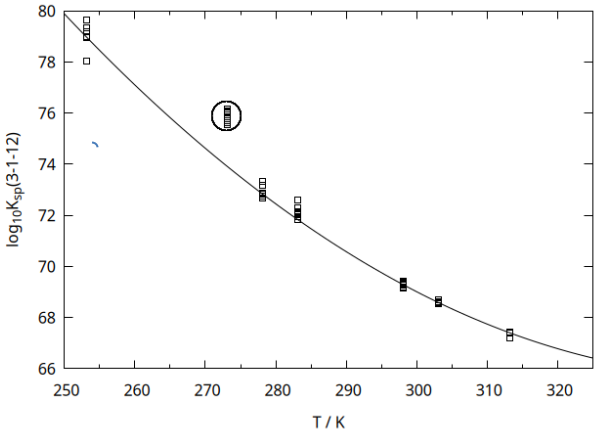

Figure 3: Solubility constants ($\log_{10}K_{sp}$) for the 3-1-12 phase depending on temperature. Circled data: 273 K values from [OCO1927] not included into the fit. Line: fit to equation (4) with the parameters from Table 2.

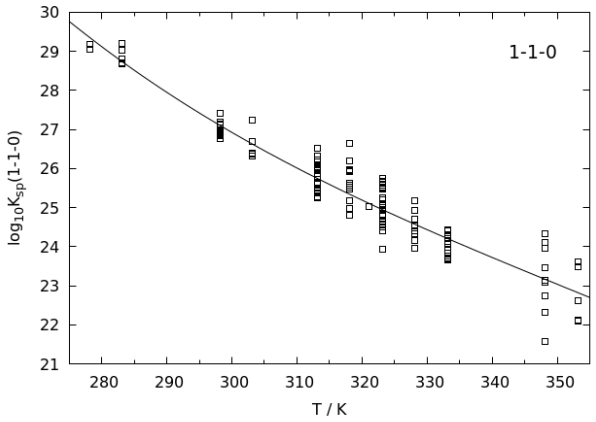

Figure 4: Solubility constants ($\log_{10}K_{sp}$) for the 1-1-0 phase depending on temperature. Line: fit to equation (4) with the parameters from Table 2.

Table 2: Fitting parameters for equation (4).

3-1-12 phase ($3Ca(OH)_2\cdot CaCl_2\cdot 12H_2O$)	
A	= 247.886
B	= -1.0509
C	= 0.00151548
D = E = F	= 0
1-1-0 phase ($Ca(OH)_2\cdot CaCl_2$)	
A	= 1624.55
B	= 1.96624
C	= -0.00143276
D = E	= 0
F	= -360.909

The data from Table 2 were entered into the THEREDA database and are available for calculations.

With this work, THEREDA now contains the correct phase stoichiometries for calcium hydroxide chlorides.

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A Appendix

Table A-1: Solubilities from literature and calculated solubility constants for Calcium Hydroxide Chlorides. Solubilities from original sources recalculated towards molalities of $CaCl_2$ and $Ca(OH)_2$. Solid phases recalculated to $xCaCl_2{\cdot}yCa(OH)_2{\cdot}zH_2O$ stoichiometries where possible. $Log_{10}(K_{sp})$ calculated via PHREEQC using THEREDA parameters as entered in release 2020. Solubility data of pure $Ca(OH)_2$ and $CaCl_2{\cdot}xH_2O$ investigated in literature are omitted here.

literature	T(K)	$CaCl_2$ (mol/kg H_2O)	$Ca(OH)_2$ (mol/kg H_2O)	solid phase	log_{10} (K_{sp}(3-1-12))	log_{10} (K_{sp}(1-1-0))
VOL/LAT1957	253.15	2.312	0.0153	Ice + 3-1-12	78.967	-
VOL/LAT1957	253.15	2.573	0.0104	3-1-12	78.043	-
VOL/LAT1957	253.15	3.560	0.0151	3-1-12	79.191	-
VOL/LAT1957	253.15	4.398	0.0181	(3-1-12)?	79.649	-
VOL/LAT1957	253.15	4.581	0.0143	3-1-12	78.999	-
VOL/LAT1957	253.15	4.627	0.0164	3-1-12 + $CaCl_2{\cdot}6H_2O$	79.345	-
OCO1927	273.15 [a]	0.659	0.0414	$Ca(OH)_2$ + 3-1-13	75.542	-
OCO1927	273.15 [a]	0.743	0.0410	3-1-13	75.619	-
OCO1927	273.15 [a]	1.026	0.0370	3-1-13	75.639	-
OCO1927	273.15 [a]	1.290	0.0351	3-1-13	75.708	-
OCO1927	273.15 [a]	1.618	0.0345	3-1-13	75.865	-
OCO1927	273.15 [a]	1.902	0.0329	3-1-13	75.868	-
OCO1927	273.15 [a]	2.257	0.0330	3-1-13	75.993	-
OCO1927	273.15 [a]	2.666	0.0335	3-1-13	76.087	-
OCO1927	273.15 [a]	3.106	0.0341	3-1-13	76.096	-
OCO1927	273.15 [a]	3.511	0.0342	3-1-13	75.990	-
OCO1927	273.15 [a]	3.815	0.0386	3-1-13	76.150	-
OCO1927	273.15 [a]	4.845	0.0522	3-1-13	76.028	-
MAK/VOL1954	278.15	0.739	0.0220	$Ca(OH)_2$ + 3-1-12	72.734	-
MAK/VOL1954	278.15	1.122	0.0198	3-1-12	72.813	-
MAK/VOL1954	278.15	1.423	0.0172	3-1-12	72.657	-
MAK/VOL1954	278.15	2.151	0.0167	3-1-12	72.873	-
MAK/VOL1954	278.15	3.691	0.0210	3-1-12	73.174	-
MAK/VOL1954	278.15	4.810	0.0332	3-1-12	73.310	-
MAK/VOL1954	278.15	5.213	0.0406	3-1-12 + 1-1-1	73.259	29.501
MAK/VOL1954	278.15	5.309	0.0215	1-1-1	-	29.063
MAK/VOL1954	278.15	5.507	0.0196	1-1-1 + $CaCl_2{\cdot}6H_2O$	-	29.169
MAK/VOL1954	283.15	1.032	0.0226	$Ca(OH)_2$ + 3-1-12	71.817	-
MAK/VOL1954	283.15	1.245	0.0215	3-1-12	71.838	-
MAK/VOL1954	283.15	2.017	0.0198	3-1-12	71.946	-
MAK/VOL1954	283.15	3.015	0.0216	3-1-12	72.123	-
MAK/VOL1954	283.15	4.038	0.0294	3-1-12	72.283	-
MAK/VOL1954	283.15	5.107	0.0487	3-1-12 + 1-1-1	72.248	28.993
MAK/VOL1954	283.15	5.210	0.0341	1-1-1	-	28.794
MAK/VOL1954	283.15	5.508	0.0218	1-1-1	-	28.675

Table A-1 (continued)

literature	T(K)	$CaCl_2$ (mol/kg H_2O)	$Ca(OH)_2$ (mol/kg H_2O)	solid phase	$\log_{10}$ (K_{sp}(3-1-12))	$\log_{10}$ (K_{sp}(1-1-0))
MAK/VOL1954	283.15	5.768	0.0177	1-1-1 + $CaCl_2 \cdot 6H_2O$	-	28.718
MIL1918	283.15	1.650	0.0215	$Ca(OH)_2$ + 3-1-13	72.039	-
MIL1918	283.15	1.618	0.0215	$Ca(OH)_2$ + 3-1-13	72.026	-
MIL1918	283.15	3.220	0.0267	3-1-13	72.583	-
MIL1918	283.15	4.322	0.0304	3-1-13	72.093	-
MIL1918	283.15	4.777	0.0383	3-1-13	72.126	-
MIL1918	283.15	5.067	0.0421	3-1-13 + 1-1-1	71.947	28.841
MIL1918	283.15	5.065	0.0421	3-1-13 + 1-1-1	71.950	28.839
MIL1918	283.15	5.586	0.0307	1-1-1	-	29.024
MIL1918	283.15	5.640	0.0366	1-1-1	-	29.214
LUN/ZAH1892	293.15	2.253	0.0351	“Ca-Oxychloride”	-	-
LUN/ZAH1892	293.15	3.004	0.0322	“Ca-Oxychloride”	-	-
LUN/ZAH1892	293.15	3.862	0.0324	“Ca-Oxychloride”	-	-
HAU/SCH2019	298.15	2.04	0.0334	$Ca(OH)_2$ + 3-1-12	69.422	-
HAU/SCH2019	298.15	2.37	0.0323	3-1-12	69.299	-
HAU/SCH2019	298.15	2.55	0.0342	3-1-12	69.398	-
HAU/SCH2019	298.15	2.75	0.0333	3-1-12	69.262	-
HAU/SCH2019	298.15	3.05	0.0363	3-1-12	69.333	-
HAU/SCH2019	298.15	3.19	0.0354	3-1-12	69.186	-
HAU/SCH2019	298.15	3.55	0.0411	3-1-12	69.292	-
HAU/SCH2019	298.15	3.55	0.0391	3-1-12	69.168	-
HAU/SCH2019	298.15	3.98	0.0464	3-1-12	69.178	-
HAU/SCH2019	298.15	4.02	0.0494	3-1-12	69.288	-
HAU/SCH2019	298.15	4.57	0.0671	3-1-12	69.332	-
HAU/SCH2019	298.15	4.89	0.0371	1-1-0	-	26.928
HAU/SCH2019	298.15	5.06	0.0286	1-1-0	-	26.839
HAU/SCH2019	298.15	5.42	0.0222	1-1-0	-	26.881
HAU/SCH2019	298.15	5.44	0.0188	1-1-0	-	26.756
HAU/SCH2019	298.15	5.87	0.0149	1-1-0	-	26.842
HAU/SCH2019	298.15	5.9	0.0155	1-1-0	-	26.894
HAU/SCH2019	298.15	6.2	0.0120	1-1-0	-	26.862
HAU/SCH2019	298.15	6.32	0.0121	1-1-0	-	26.940
HAU/SCH2019	298.15	6.5	0.0108	1-1-0	-	26.947
HAU/SCH2019	298.15	6.94	0.0103	1-1-0	-	27.144
MIL1918	298.15	2.002	0.0323	$Ca(OH)_2$ + 3-1-13	69.339	-
MIL1918	298.15	1.983	0.0331	$Ca(OH)_2$ + 3-1-13	69.401	-
MIL1918	298.15	2.403	0.0333	3-1-13	69.369	-
MIL1918	298.15	2.820	0.0342	3-1-13	69.299	-
MIL1918	298.15	2.903	0.0347	3-1-13	69.297	-
MIL1918	298.15	3.577	0.0424	3-1-13	69.346	-
MIL1918	298.15	3.787	0.0457	3-1-13	69.339	-
MIL1918	298.15	4.387	0.0598	3-1-13	69.307	-
MIL1918	298.15	4.497	0.0657	3-1-13 + 1-1-1	69.384	27.083

Table A-1 (continued)

literature	T(K)	$CaCl_2$ (mol/kg H_2O)	$Ca(OH)_2$ (mol/kg H_2O)	solid phase	$\log_{10}$ (K_{sp}(3-1-12))	$\log_{10}$ (K_{sp}(1-1-0))
MIL1918	298.15	4.602	0.0686	3-1-13 + 1-1-1	69.338	27.197
MIL1918	298.15	4.729	0.0471	1-1-1	-	27.000
MIL1918	298.15	5.672	0.0174	1-1-1	-	26.845
MIL1918	298.15	6.350	0.0146	1-1-1	-	27.116
MIL1918	298.15	7.170	0.0096	1-1-1	-	27.200
MIL1918	298.15	7.230	0.0071	1-1-1 + $CaCl_2{\cdot}6H_2O$	-	26.972
MIL1918	298.15	7.285	0.0116	1-1-1 + $CaCl_2{\cdot}6H_2O$	-	27.416
SCH/FIG1911	298.15	2.002	0.0323	$Ca(OH)_2$ + 4-1-10	69.338	-
SCH/FIG1911	298.15	1.983	0.0331	4-1-10	69.401	-
SCH/FIG1911	298.15	2.403	0.0333	4-1-10	69.365	-
SCH/FIG1911	298.15	2.820	0.0342	4-1-10	69.301	-
SCH/FIG1911	298.15	2.903	0.0347	4-1-10	69.297	-
SCH/FIG1911	298.15	3.577	0.0424	4-1-10	69.347	-
SCH/FIG1911	298.15	3.787	0.0457	4-1-10	69.336	-
SCH/FIG1911	298.15	4.387	0.0598	4-1-10	69.307	-
SCH/FIG1911	298.15	4.497	0.0657	4-1-10	69.384	-
SCH/FIG1911	298.15	4.602	0.0686	4-1-10 + 1-1-0	69.338	26.372
SCH/FIG1911	298.15	4.729	0.0471	1-1-0	-	27.416
SCH/FIG1911	298.15	5.672	0.0174	1-1-0	-	27.196
SCH/FIG1911	298.15	6.350	0.0146	1-1-0	-	27.000
SCH/FIG1911	298.15	7.205	0.0097	1-1-0	-	26.848
SCH/FIG1911	298.15	7.230	0.0071	1-1-0 + $CaCl_2{\cdot}6H_2O$	-	27.115
SCH/FIG1911	298.15	7.285	0.0116	1-1-0 + $CaCl_2{\cdot}6H_2O$	-	27.201
MAK/VOL1954	303.15	2.349	0.0392	$Ca(OH)_2$ + 3-1-12	68.557	-
MAK/VOL1954	303.15	2.777	0.0425	3-1-12	68.595	-
MAK/VOL1954	303.15	3.274	0.0480	3-1-12	68.590	-
MAK/VOL1954	303.15	4.273	0.0739	3-1-12	68.610	-
MAK/VOL1954	303.15	4.416	0.0787	3-1-12	68.568	-
MAK/VOL1954	303.15	4.446	0.0870	3-1-12 + 1-1-1	68.758	26.740
MAK/VOL1954	303.15	4.626	0.0450	1-1-1	-	26.365
MAK/VOL1954	303.15	5.071	0.0296	1-1-1	-	26.393
MAK/VOL1954	303.15	5.705	0.0176	1-1-1	-	26.316
MAK/VOL1954	303.15	6.500	0.0163	1-1-1	-	26.694
MAK/VOL1954	303.15	7.872	0.0152	1-1-1 + $CaCl_2{\cdot}4H_2O$	-	27.241
MOZ/ZOZ1983	303.15	2.376	0.0417	$Ca(OH)_2$ + 3-1-12	68.702	-
HAU/SCH2019	313.15	3.98	0.1020	3-1-12	67.217	-
HAU/SCH2019	313.15	4.14	0.1228	3-1-12	67.427	-
HAU/SCH2019	313.15	4.18	0.1245	3-1-12	67.405	-
HAU/SCH2019	313.15	4.38	0.0762	1-1-0	-	25.620
HAU/SCH2019	313.15	4.85	0.0377	1-1-0	-	25.383
HAU/SCH2019	313.15	5.30	0.0232	1-1-0	-	25.261
HAU/SCH2019	313.15	5.75	0.0173	1-1-0	-	25.269
HAU/SCH2019	313.15	6.27	0.0143	1-1-0	-	25.372

Table A-1 (continued)

literature	T(K)	$CaCl_2$ (mol/kg H_2O)	$Ca(OH)_2$ (mol/kg H_2O)	solid phase	$\log_{10}$ (K_{sp}(3-1-12))	$\log_{10}$ (K_{sp}(1-1-0))
HAU/SCH2019	313.15	6.78	0.0126	1-1-0	-	25.495
HAU/SCH2019	313.15	7.19	0.0119	1-1-0	-	25.609
HAU/SCH2019	313.15	7.89	0.0112	1-1-0	-	25.793
HAU/SCH2019	313.15	8.09	0.0129	1-1-0	-	25.968
HAU/SCH2019	313.15	8.85	0.0123	1-1-0	-	26.104
LUN/ZAH1892	313.15	2.994	0.0583	"Ca-Oxychloride"	-	-
LUN/ZAH1892	313.15	3.846	0.0729	"Ca-Oxychloride"	-	-
MAK/VOL1954	313.15	4.287	0.1485	$Ca(OH)_2$ + 1-1-1	-	26.018
MAK/VOL1954	313.15	4.351	0.1127	1-1-1	-	25.880
MAK/VOL1954	313.15	4.755	0.0434	1-1-1	-	25.435
MAK/VOL1954	313.15	4.591	0.0204	1-1-1	-	25.446
MAK/VOL1954	313.15	7.170	0.0121	1-1-1	-	25.617
MAK/VOL1954	313.15	8.411	0.0157	1-1-1	-	26.212
MAK/VOL1954	313.15	8.821	0.0160	1-1-1 + $CaCl_2{\cdot}4H_2O$	-	26.319
MAK/VOL1954	313.15	8.779	0.0160	1-1-1 + $CaCl_2{\cdot}4H_2O$	-	26.310
MIL1918	313.15	4.265	0.1610	$Ca(OH)_2$ + 1-1-1	-	26.052
MIL1918	313.15	4.256	0.1508	$Ca(OH)_2$ + 1-1-1	-	26.006
MIL1918	313.15	4.249	0.1531	$Ca(OH)_2$ + 1-1-1	-	26.011
MIL1918	313.15	9.009	0.0196	1-1-1 + $CaCl_2{\cdot}4H_2O$	-	26.520
MAK/VOL1954	318.15	4.147	0.1509	$Ca(OH)_2$ + 1-1-1	-	25.480
MAK/VOL1954	318.15	4.307	0.0640	1-1-1	-	24.987
MAK/VOL1954	318.15	5.090	0.0275	1-1-1	-	24.804
MAK/VOL1954	318.15	5.914	0.0201	1-1-1	-	24.990
MAK/VOL1954	318.15	6.998	0.0144	1-1-1	-	25.177
MAK/VOL1954	318.15	9.253	0.0192	1-1-1	-	25.970
MAK/VOL1954	318.15	10.376	0.0232	1-1-1 + $CaCl_2{\cdot}2H_2O$	-	26.196
MIL1918	318.15	4.224	0.1637	$Ca(OH)_2$ + 1-1-1	-	25.581
MIL1918	318.15	4.270	0.1677	$Ca(OH)_2$ + 1-1-1	-	25.625
MIL1918	318.15	5.075	0.1238	1-1-1	-	25.929
MIL1918	318.15	5.557	0.0199	1-1-1	-	24.798
MIL1918	318.15	6.893	0.0233	1-1-1	-	25.537
MIL1918	318.15	9.810	0.0175	1-1-1	-	25.948
MIL1918	318.15	11.958	0.0503	1-1-1 + $CaCl_2{\cdot}2H_2O$	-	26.643
MIL1918	321.15	4.228	0.1142	$Ca(OH)_2$ + 1-1-3…4	-	-
MIL1918	321.15	4.188	not det.	$Ca(OH)_2$ + 1-1-3…4	-	-
MIL1918	321.15	4.431	0.0854	1-1-1 + 1-1-3…4	-	25.019
MAK/VOL1954	323.15	4.242	0.1440	$Ca(OH)_2$ + 1-1-1	-	25.082
MAK/VOL1954	323.15	4.357	0.1209	1-1-1	-	25.043
MAK/VOL1954	323.15	4.508	0.0895	1-1-1	-	24.930
MAK/VOL1954	323.15	5.152	0.0340	1-1-1	-	24.564
MAK/VOL1954	323.15	5.802	0.0222	1-1-1	-	24.554
MAK/VOL1954	323.15	6.122	0.0204	1-1-1	-	24.633
MAK/VOL1954	323.15	8.885	0.0215	1-1-1	-	25.497

Table A-1 (continued)

literature	T(K)	$CaCl_2$ (mol/kg H_2O)	$Ca(OH)_2$ (mol/kg H_2O)	solid phase	log_{10} (K_{sp}(3-1-12))	log_{10} (K_{sp}(1-1-0))
MAK/VOL1954	323.15	10.517	0.0263	1-1-1 + $CaCl_2 \cdot 2H_2O$	-	25.759
MIL1918	323.15	3.819	0.0922	$Ca(OH)_2$ + 1-1-3…4	-	-
MIL1918	323.15	3.816	0.1319	1-1-3…4	-	-
MIL1918	323.15	4.211	0.1236	1-1-3…4	-	-
MIL1918	323.15	4.903	0.0292	1-1-3…4	-	-
MIL1918	323.15	5.290	0.032	1-1-1 + 1-1-3…4	-	24.591
MIL1918	323.15	5.263	0.0413	1-1-1 + 1-1-3…4	-	24.781
MIL1918	323.15	5.286	0.0351	1-1-1	-	24.664
MIL1918	323.15	5.872	0.0203	1-1-1	-	24.514
MIL1918	323.15	7.551	0.0167	1-1-1	-	24.997
MIL1918	323.15	7.813	0.0153	1-1-1	-	24.997
MIL1918	323.15	8.057	0.0115	1-1-1	-	24.817
MIL1918	323.15	8.578	0.0160	1-1-1	-	25.205
MIL1918	323.15	10.601	0.0186	1-1-1 + $CaCl_2 \cdot 2H_2O$	-	25.478
MIL1918	323.15	10.623	0.0264	1-1-1 + $CaCl_2 \cdot 2H_2O$	-	25.758
REP/LEG1938*	323.15	10.320	0.0200	1-1-1 + $CaCl_2 \cdot 2H_2O$	-	25.537
REP/LEG1938*	323.15	5.332	0.0327	$CaCl_2 \cdot CaO \cdot 5H_2O$ + 1-1-1	-	24.629
REP/LEG1938*	323.15	3.892	0.0924	$Ca(OH)_2$ + $CaCl_2 \cdot CaO \cdot 5H_2O$	-	-
TRA/POP1961**[b]	323.15	3.942	0.0399	$Ca(OH)_2$ + 1-1-1	-	23.942
TRA/POP1961**[b]	323.15	4.604	0.0421	1-1-1	-	24.416
TRA/POP1961**[b]	323.15	5.643	0.0396	1-1-1	-	24.945
TRA/POP1961**[b]	323.15	6.324	0.0396	1-1-1	-	25.258
TRA/POP1961**[b]	323.15	7.817	0.0308	1-1-1	-	25.570
TRA/POP1961**[b]	323.15	9.105	0.0261	1-1-1	-	25.685
TRA/POP1961**[b]	323.15	9.924	0.0227	1-1-1 + $CaCl_2 \cdot 2H_2O$	-	25.638
MAK/VOL1954	328.15	4.241	0.1520	$Ca(OH)_2$ + 1-1-1	-	24.705
MAK/VOL1954	328.15	4.319	0.1064	1-1-1	-	24.522
MAK/VOL1954	328.15	4.517	0.0753	1-1-1	-	24.396
MAK/VOL1954	328.15	4.895	0.0417	1-1-1	-	24.163
MAK/VOL1954	328.15	4.603	0.0245	1-1-1	-	23.964
MAK/VOL1954	328.15	6.901	0.0167	1-1-1	-	24.332
MAK/VOL1954	328.15	7.526	0.0174	1-1-1	-	24.563
MAK/VOL1954	328.15	8.933	0.0188	1-1-1	-	24.927
MAK/VOL1954	328.15	10.032	0.0171	1-1-1	-	24.935
MAK/VOL1954	328.15	10.997	0.0240	1-1-1 + $CaCl_2 \cdot 2H_2O$	-	25.180
HAU/SCH2019	333.15	4.41	0.0718	1-1-0	-	23.906
HAU/SCH2019	333.15	4.88	0.0390	1-1-0	-	23.704
HAU/SCH2019	333.15	5.36	0.0276	1-1-0	-	23.678
HAU/SCH2019	333.15	5.82	0.0209	1-1-0	-	23.669
HAU/SCH2019	333.15	6.33	0.0178	1-1-0	-	23.754
HAU/SCH2019	333.15	6.77	0.0159	1-1-0	-	23.828

Table A-1 (continued)

literature	T(K)	$CaCl_2$ (mol/kg H_2O)	$Ca(OH)_2$ (mol/kg H_2O)	solid phase	$\log_{10}$ (K_{sp}(3-1-12))	$\log_{10}$ (K_{sp}(1-1-0))
HAU/SCH2019	333.15	7.27	0.0155	1-1-0	-	23.972
HAU/SCH2019	333.15	7.83	0.0149	1-1-0	-	24.094
HAU/SCH2019	333.15	8.35	0.0150	1-1-0	-	24.215
HAU/SCH2019	333.15	8.84	0.0147	1-1-0	-	24.282
HAU/SCH2019	333.15	9.96	0.0150	1-1-0	-	24.397
HAU/SCH2019	333.15	11.55	0.0173	1-1-0	-	24.434
HAU/SCH2019	333.15	12.28	0.0173	1-1-0	-	24.310
MAK/VOL1954	348.15	4.011	0.1414	$Ca(OH)_2$ + 1-1-1	-	23.081
MAK/VOL1954	348.15	4.456	0.0607	1-1-1	-	22.749
MAK/VOL1954	348.15	7.830	0.0253	1-1-1	-	23.461
MAK/VOL1954	348.15	11.968	0.0378	1-1-1 + $CaCl_2 \cdot 2H_2O$	-	24.108
TRA/POP1961**[b]	348.15	4.289	0.0307	$Ca(OH)_2$ + 1-1-1	-	22.310
TRA/POP1961**[b]	348.15	4.325	0.0404	$Ca(OH)_2$ + 1-1-1	-	21.583
TRA/POP1961**[b]	348.15	6.169	0.0392	1-1-1	-	23.147
TRA/POP1961**[b]	348.15	7.967	0.0158	1-1-1	-	23.952
TRA/POP1961**[b]	348.15	8.514	0.0344	1-1-1	-	24.334
TRA/POP1961**[b]	348.15	9.576	0.0446	2-1-1	-	(23.746)
TRA/POP1961**[b]	348.15	10.515	0.0627	2-1-1	-	(24.177)
TRA/POP1961**[b]	348.15	10.997	0.0240	2-1-1	-	(24.261)
TRA/POP1961**[b]	348.15	12.150	0.0381	2-1-1 + $CaCl_2 \cdot 2H_2O$	-	(23.974)
TRA/POP1961**[b]	353.15	4.364	0.0424	$Ca(OH)_2$ + 1-1-1	-	22.097
TRA/POP1961**[b]	353.15	4.779	0.0327	1-1-1	-	22.121
TRA/POP1961**[b]	353.15	6.379	0.0235	1-1-1	-	22.608
TRA/POP1961**[b]	353.15	8.024	0.0409	1-1-1	-	23.608
TRA/POP1961**[b]	353.15	9.018	0.0265	2-1-1	-	(23.481)
TRA/POP1961**[b]	353.15	9.919	0.0173	2-1-1	-	(23.258)
TRA/POP1961**[b]	353.15	11.152	0.0402	2-1-1	-	(24.007)
TRA/POP1961**[b]	353.15	11.988	0.0227	2-1-1	-	(23.519)

[a] from the graphical representation of solubility data in Figure 1 the suspicion arises that experiments might have been carried out at 298 K rather than 273 K.

[b] Data show an unusual scattering (cf. Figure 2)

* values taken as cited in [ZDA/LYC1953]

** valuesd taken as cited in [KOG/OGO1970]

(end of table)