

Estimation of the Solubility Constant of Calcite, Aragonite, and Vaterite at 25°C Based on Primary Data Using the *Pitzer* Ion Interaction Approach

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Summary. Experimentally determined values of the solubility constant of anhydrous calcium carbonate species were compiled from primary literature. The data were processed using a least-squares technique and the activity coefficients were calculated using the *Pitzer* ion interaction model. It was shown that the literature data considered can be divided into two data sets which are internally consistent, but mutually inconsistent. The first data set was consistent with the existence of the CaHCO_3^+ ion pair, while the second data set was not. It was assumed that the difference between the two data sets might be due to surface charge effects.

Keywords. Solubility; Calcium carbonate; Thermodynamics; Salt effect; Ion interaction.

Introduction

Despite the many efforts and the current advanced ionic interaction models available, there is still no universally accepted value of the solubility constant of the anhydrous calcium carbonate varieties. However, due to its numerous applications, this constant is of vital importance in many fields, ranging from geochemistry to industrial processes.

The first efforts to quantify calcium carbonate solubility in aqueous systems date back to the middle of the 19th century [1, 2]. A large amount of data was generated before the development of advanced and accurate models of ion interactions of which the *Pitzer* model was the most straightforward [3, 4]. Without these it is hardly possible to derive thermodynamic data from nonideal systems such as the $\text{CaCO}_3(\text{s})\text{--H}_2\text{O}(\text{l})\text{--CO}_2(\text{g})$ system. An additional complication has

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Dedicated to Prof. Dr. H. Gamsjäger on the occasion of his 70th birthday

been the need for ancillary data such as the aqueous solubility of $\text{CO}_2(\text{g})$. Updates of these properties need evidently to be incorporated in the calculation of the calcium carbonate solubility constant as well. However, when properties from different sources are used in the calculation, their overall internal consistency must be guarded.

The most comprehensive primary data set is provided by *Plummer and Busenberg* [5]. They calculated ion activity coefficients with the extended *Debye-Hückel* equation, and accounted for ion interactions only by means of the formation constants of the metal-carbonate ion pairs CaCO_3^0 and CaHCO_3^+ . It was concluded that both constants are required for a correct description of the solubility data. This view was shared by *Sass et al.* [6]. However, these data sets have never been processed using the *Pitzer* model.

Vanderdeelen et al. [7] used a least-squares technique for the simultaneous assessment of the solubility constant of calcite and the formation constant of the ion pairs CaCO_3^0 and CaHCO_3^+ . Activity coefficients were calculated with the *Davies* equation. The data set used was compiled from *Frear and Johnson* [8], *Shternina and Frolova* [9], and *Yanat'eva* [10]. They concluded that the solubility data were not consistent with the existence of the CaHCO_3^+ ion pair. This view was also supported by *Jacobson and Langmuir* [11], *Millero et al.* [12], and *Harvie et al.* [13].

Taking account of the CaHCO_3^+ ion pair will influence the estimate of the solubility constant, K_S , by 0.05 log-units [11], it is concluded that in the analysis of the solubility data this ion pair cannot be neglected. According to *Pitzer et al.* [14], ion pairs like CaHCO_3^+ , with a formation constant $<10^3$, will be essentially fitted by the binary cation-anion interaction coefficient, B_{MX} . More stable ion pairs, like CaCO_3^0 , should be expressed by a conventional formation constant, K_{CaCO_3} .

The aim of this study was to update the approach of *Vanderdeelen et al.* [7] by introducing the *Pitzer* model for the calculation of the activity coefficients and using a least-squares technique to estimate both K_S and the coefficient $\beta^{(0)}$ of the binary $\text{Ca}^{2+}-\text{HCO}_3^-$ interaction coefficient, B_{MX} .

Results and Discussion

Aragonite Solubility Data

Plummer and Busenberg [5] carefully measured calcite, aragonite, and vaterite solubilities in pure water at various temperatures and $\text{CO}_2(\text{g})$ partial pressures. The most comprehensive data set at 25°C refers to aragonite. This data set was used to estimate the solubility constant of aragonite, K_S , and the coefficient $\beta^{(0)}$ of the binary $\text{Ca}^{2+}-\text{HCO}_3^-$ interaction parameter, B_{MX} . The coefficient $\beta^{(1)}$, displaying the ionic strength (I) dependence of B_{MX} , could not be estimated because $I < 0.03 \text{ mol kg}^{-1}$ for the entire data set. Therefore, $\beta^{(1)}$ was set equal to zero. The formation constant, K_{CaCO_3} , was determined by several researchers [5, 11, 13]. The results are less than 0.1 log-units apart and do not influence the estimates of K_{CaCO_3} , $\beta^{(0)}$, and $\beta^{(1)}$ significantly. The values cluster around the value obtained from thermodynamic data by *Königsberger et al.* [15] ($10^{3.189}$) and we used this value in our further calculations. The optimum parameter set was assumed to be

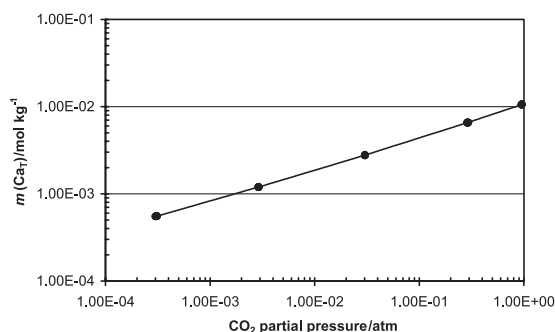


Fig. 1. Calcium molality versus CO_2 partial pressure in the aragonite– H_2O – CO_2 system; dots are experimental data of Ref. [5]; straight line is model prediction according to least-squares optimisation

the one for which the sum of squares of the deviations between the measured molalities of Ca_T , $m(\text{Ca}_T)_{\text{exp}}$, and the fitted molalities of Ca_T , $m(\text{Ca}_T)_{\text{fit}}$, on log scale was minimal. The optimum was found at $\log(K_S) = -8.331 \pm 0.003$ in combination with $\beta^{(0)} = -1.44 \pm 0.16$. Note that the uncertainties presented in this paper are estimates based on a linearization of the model, and may be underestimated when the model is strongly nonlinear and the parameters are strongly correlated. Figure 1 shows predictions of $m(\text{Ca}_T)$ versus $\text{CO}_2(\text{g})$ partial pressure, together with the experimental data. The agreement seems to be excellent, with a standard deviation of about 0.5%. The value of $\log(K_S)$ agrees well with *Plummer* and *Busenberg's* estimate (-8.332 ± 0.0077), and is slightly above the value calculated from their regression equation (-8.336). The value of $\beta^{(0)}$ is below the estimates of both *Pitzer et al.* ($\beta^{(0)} = 0.28$; $\beta^{(1)} = 0.3$) and *Harvie et al.* ($\beta^{(0)} = 0.4$; $\beta^{(1)} = 2.977$) [13, 14]. A negative $\beta^{(0)}$ value means that the ions lower each other's activity coefficient, which indicates ion association [13, 14]. Such a good fit between the model and the data is not obtained across the entire $\text{CO}_2(\text{g})$ partial pressure range when the β values of *Harvie et al.* [13] or *Pitzer et al.* [14] are used. This indicates that these parameters are not consistent with the aragonite solubility data of *Plummer* and *Busenberg* [5].

Calcite Solubility Data: $m(\text{Ca}_T)$ Versus $p(\text{CO}_2)$

Next, we used the model to estimate the value of K_S of calcite based on the experimental data of *Plummer* and *Busenberg* [5], *Sass et al.* [6], and *Wolf et al.* [16]. The parameter $\beta^{(0)}$ was kept constant at -1.44 with a resulting $\log(K_S) = -8.485 \pm 0.009$. The standard deviation between the experimental data and the model is about 1.6%. The fit is shown in Fig. 2 (full line, black dots). Data from the three references are clearly internally consistent and also with regard to the parameter $\beta^{(0)}$ derived from the aragonite data.

Figure 2 also contains experimental data of a number of other studies (empty markers: Refs. [8–10, 17, 18]). They show systematically higher solubilities than the model. The difference is negligible at high CO_2 pressure, but reaches 6–7% at low CO_2 pressure, largely exceeding the precision of the solubility measurements.

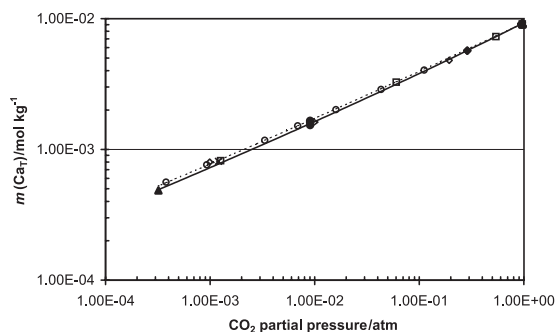


Fig. 2. Calcium molality versus CO_2 partial pressure in the calcite– H_2O – CO_2 system; black markers are experimental data of Refs. [5] (diamonds), [6] (triangles), and [16] (dots); empty markers are experimental data of Refs. [8] (dots), [9] (squares), [10] (crosses), [17] (diamonds), and [18] (triangles); full line is model prediction with $\log(K_S)=-8.485$, $\beta^{(0)}=-1.44$, $\beta^{(1)}=0$; dotted line is model prediction with $\log(K_S)=-8.401$, $\beta^{(0)}=1.72$, $\beta^{(1)}=0$

The standard deviation between those data points and the model is 4.6%. Clearly, the two data sets are inconsistent.

Vaterite Solubility Data

The vaterite solubility data set at 25°C is limited to only two experiments by *Plummer and Busenberg* [5]. When the model is applied to those data, again assuming $\beta^{(0)}=-1.44$, a value of $\log(K_S)=-7.927$ is obtained. This is markedly lower than their own estimate amounting to -7.902 from the experimental data and to -7.914 from their regression model. Even at these low ionic strengths the choice of the model for calculating the ion activity coefficient influences the result of the calculation.

Calcite Solubility Data: $m(\text{Ca}_T)$ Versus pH

Grèzes and Basset [19], *Picknett* [20, 21], and *Le Guyader et al.* [22] investigated the solubility of calcite in closed systems with different CO_2 contents. In these conditions the analytical molalities of calcium, $m(\text{Ca}_T)$, were determined as a function of pH . The advantage of this methodology is that a broad range of solubilities is reached, which will subsequently allow a more accurate estimation of K_S and $\beta^{(0)}$. A disadvantage is a potential measurement bias of the pH . The parameters generating the best fit of the data set were estimated by minimizing the sum of squares of the difference between the measured and the calculated values of $\ln(m(\text{Ca}_T))$. The following values were obtained: $\log(K_S)=-8.401\pm 0.012$ and $\beta^{(0)}=1.72\pm 1.68$. The results are shown in Fig. 3, together with the predictions based on the calcite parameters obtained in the previous section. While the three studies evaluated in this section are internally consistent, they fail with the data of Refs. [5, 6, 16]. We tested the consistency with the other $m(\text{Ca}_T)$ – $p(\text{CO}_2)$ data set, by making predictions of $m(\text{Ca}_T)$ versus $p(\text{CO}_2)$ based on the parameters estimated in this section. The result is shown in the dotted line in Fig. 2. Clearly, the data of Refs. [8–10, 17, 18] are consistent with the $m(\text{Ca}_T)$ – pH data.

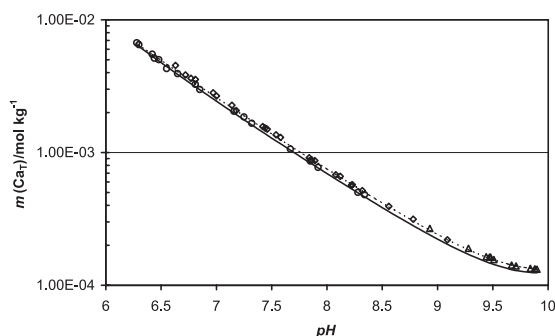


Fig. 3. Calcium molality versus pH in the calcite–H₂O–CO₂ system; dots are experimental data of Refs. [19] (triangles), [20, 21] (diamonds), and [22] (dots); full line is model prediction with $\log(K_S)=-8.485$, $\beta^{(0)}=-1.44$, $\beta^{(1)}=0$; dotted line is model prediction with $\log(K_S)=-8.401$, $\beta^{(0)}=1.72$, $\beta^{(1)}=0$

Consistency Issue

From the previous sections it results that the literature data on calcite solubility can be subdivided into two highly self-consistent but mutually inconsistent data sets. The first set consists of data of *Plummer and Busenberg* [5], *Sass et al.* [6], and *Wolf et al.* [16]. These data sets are also consistent with the aragonite data set of *Plummer and Busenberg*, and with the existence of a CaHCO_3^+ ion pair (negative $\beta^{(0)}$).

The second data set consists of the data of Refs. [8–10, 17–22], limited to the calcite–H₂O–CO₂ system, and is inconsistent with a CaHCO_3^+ ion pair. *Harvie et al.* [13] remarks that some data sets are inconsistent with a CaHCO_3^+ ion pair but become consistent with such a species at NaCl molalities exceeding 1 mol kg^{-1} .

It is hard to believe that one of these data sets is unreliable and should be excluded. *Sass et al.* [6] suggested that the difference between their data set and the previous data sets is due to a difference in particle size. They observed that acid leaching of the calcite reduced the solubility at low ionic strength, and attributed this to the dissolution of the finest fraction of the calcite particles. *Plummer and Busenberg* [5] found that recrystallisation of the calcite was highly required in order to obtain precise and accurate determinations.

Particle size effects do not explain the ionic strength dependence of a solubility increase. This ionic strength dependence should point toward an electric double layer effect. When particles suspended in water are electrically charged, a diffuse layer of counter-ions surrounding the particle is created. The ionic strength in this diffuse layer exceeds the ionic strength of the bulk liquid. Double layers largely vanish when the ionic strength of the solution is increased. We therefore hypothesize that freshly suspended calcite particles are charged when suspended in CO₂-free water, and that this surface charge can be removed by acid leaching or by recrystallisation. We also hypothesize that the diffuse layer surrounding a charged particle can increase the solubility. A possible mechanism is the decrease of the activity coefficient of Ca^{2+} and CO_3^{2-} in the diffuse layer due to the high local ionic strength. These suggestions tend to explain the existence of two internally

Table 1. Recommended values of $\log(K_S)$, $\beta^{(0)}$, and $\beta^{(1)}$ and $\Delta G_{f,298.15\text{K}}^\circ$ of calcite, aragonite, and vaterite

Polymorphic variety	$\log(K_S)$	$\beta^{(0)}$	$\beta^{(1)}$	$\Delta G_{f,298.15\text{K}}^\circ$ (kJ mol ⁻¹)	Consistent with refs.
Calcite	-8.485	-1.44	0	-1235.00	[5, 6, 16]
	-8.401	1.72	0	-1234.52	[8-10, 17-22]
	-8.407	0.28	0.3	-1234.55	[8-10, 17-22]
	-8.395	0.40	2.977	-1234.49	[8-10, 17-22]
Aragonite	-8.331	-1.44	0	-1234.12	[5]
	-8.283	1.72	0	-1233.85	-
	-8.301	0.28	0.3	-1233.95	-
	-8.267	0.40	2.977	-1233.75	-
Vaterite	-7.927	-1.44	0	-1231.81	-(a)
	-7.774	1.72	0	-1230.94	-(a)
	-7.836	0.28	0.3	-1231.29	-(a)
	-7.733	0.40	2.977	-1230.71	-(a)

(a) Insufficient data to test overall consistency

consistent, mutually inconsistent data sets in the literature, and also the ionic strength dependence of the disparity between the two data sets.

Recommended Solubility Constants

When thermodynamic data are published, internal consistency of the figures is more important than the absolute exactness of a single figure. We therefore present sets of thermodynamic figures (K_{CaCO_3} , $\beta^{(0)}$, and $\beta^{(1)}$) rather than individual figures. The sets are shown in Table 1. Apart from the two values of $\beta^{(0)}$ proposed in the present study, we also present solubility constants which are consistent with the values of $\beta^{(0)}$ and $\beta^{(1)}$ put forward by *Pitzer et al.* [14] and by *Harvie et al.* [13]. The proposed values of $\Delta G_{f,298.15\text{K}}^\circ$ are for use with the CODATA thermochemical values of Ca^{2+} and CO_3^{2-} .

Conclusions

Least-squares analysis of anhydrous calcium carbonate solubility determinations from literature shows that the literature data can be split up into two internally consistent but mutually inconsistent data sets. The first is consistent with the occurrence of a stable CaHCO_3^+ ion pair, while the second is inconsistent. It is assumed that the latter data set was obtained with charged calcite particles, and that this surface charge results in an increased solubility constant at low $\text{CO}_2(\text{g})$ pressure.

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