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THERMODYNAMIC ASPECTS OF THE VATERITE–CALCITE PHASE TRANSITION

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Abstract

Although vaterite is the least stable anhydrous calcium carbonate polymorph, it is formed as a metastable phase in some normal and pathological biomineralisation processes. In this work, thermodynamic aspects of the vaterite–calcite phase transition were comprehensively studied. Vaterite samples were prepared by different methods and characterised for the composition, crystal structure, specific surface and grain size. All products were identified to be pure vaterite by careful X-ray diffraction measurements. The enthalpy and Gibbs energy of transition were determined by precise calorimetric and potentiometric measurements. The reliability of the thermodynamic data for the vaterite–calcite phase transition derived from this work was shown by the use of different calorimetric methods to determine the enthalpy of transition and the independent measurements of heat capacity and entropy of vaterite. Our recommended values are $\Delta_{trs}G^* = -2.9 \pm 0.2$ kJ mol^{-1}, $\Delta_{trs}H^* = -3.4 \pm 0.2$ kJ mol^{-1} and $\Delta_{trs}S^* = -1.7 \pm 0.9$ J K^{-1} mol^{-1}, where the uncertainties are given as twice the standard deviations.

Keywords: calcite, calcium carbonate polymorphs, phase transition, thermodynamics, vaterite

Introduction

Calcium carbonate exists in three anhydrous polymorphic modifications, vaterite, aragonite and calcite. At ambient temperature and atmospheric pressure, vaterite is the least stable phase and calcite is the most stable one. As a consequence of its exceptional formation conditions and high instability, deposits of vaterite are relatively scarce in nature; e.g. vaterite has been found as a rare mineral in metamorphic rocks and sediments [1]. However, vaterite is an important phase formed in biomineralisation processes [2], it has been found in gallstones, otoliths, shells and skeletons [3–5].

Vaterite was first described as μ-$CaCO_3$ by Vater [6, 7] some 90 years ago but still remains a poorly characterised (bio-)mineral [8]. In this work, proper calorimet-

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ric and potentiometric techniques were employed to thoroughly investigate the thermodynamic properties of the vaterite–calcite phase transition. The heat capacity and entropy of vaterite were also measured independently to corroborate the improved set of thermodynamic data derived from this work.

Experimental

Synthesis of vaterite samples

Vaterite prepared in the laboratory is obtained as primary crystallisation of $CaCO_3$ from highly concentrated solutions at relatively low temperature [9]. In this work, vaterite samples named A, B, C, D and E were prepared by using five different methods; more details of the preparation techniques can be found in [10]. Sample A was synthesised by passing a rapid CO_2 stream through a stirred aqueous solution of $CaCl_2$ and NH_3 at room temperature. The preparation of sample B was similar to that of sample A, but the solution was adjusted to $pH\approx10$ during the reaction. By dropwise addition of potassium, sodium, and lithium carbonate to $CaCl_2$ solution, vaterite samples C, D and E were prepared respectively. After precipitation, all samples were washed with ethanol, filtered and dried at 85–90°C. The methods to synthesise vaterite A and D were also reported in [1].

Characterisation of vaterite samples

The crystal structure of vaterite is hexagonal [1, 11, 12] and characterised by a spherulitic morphology [13, 14] with a high number of lattice defects. These may be responsible for the problems to completely remove water and other impurities from synthetic vaterite. Therefore samples obtained from the different preparation methods can have different properties.

In this work, powder X-ray diffractometry was carried out for all samples and only characteristic peaks of vaterite were found. The thermogravimetric investigation (using a Setaram TG111) shows that in all samples there is a small residual water content between 1.3 (vaterite A) and 2.3 (vaterite D) mass%, which only disappears near the phase transition temperature. Despite the different preparation methods, all vaterite samples have the same specific surface of $8\pm1\ m^2\ g^{-1}$ (Stroehlein Instruments DEN-AR-mat 1000) and parabolic distribution of the grain size with a maximum of almost 10 μm (Lasergranulometer Coulter LS 130). However, only samples A and B have spherulitic morphology and no impurities of alkali metals. Samples C, D and E have a more star like morphology and a content of alkali metal impurities of 1.5±0.1 mass%. From all investigations, especially after the correction for the small water content, sample A seems to have all properties that are most typical of pure vaterite.

Calorimetric measurements of the vaterite – calcite transition

The thermally activated vaterite–calcite phase transition under CO_2 atmosphere at temperatures above 630 K was investigated by isothermal and non-isothermal differential scanning calorimetry. A Setaram DSC 111 was employed in this study and details were published in [10].

The phase transition activated by aqueous $CaCO_3$-saturated solution in a temperature range from 25 to 80°C was investigated using a Setaram Micro DSC II. Measurements were carried out for samples A to D at different heating rates, $0.01 \leq \beta/\mathrm{K\ min^{-1}} \leq 0.2$. Additionally, isothermal measurements for sample A were performed at 30, 35, 40 and 50°C. In every experiment, to ensure a proper saturation, the calorimetric cells were filled with 0.2 ml of a $CaCO_3$-saturated solution and 10 mg of calcite. Around 100 mg of vaterite were added to the solution and in the reference cell calcite was used instead.

To study the reaction enthalpies $\Delta_r H$ of the polymorphs at 40°C, 150 mg of either calcite or vaterite were dissolved in 80 ml of an aqueous alkaline EDTA solution (0.5 mol kg^{-1}, pH=10.3). The measurements were performed using a modified LKB 8700 calorimeter, as described in an earlier publication [15]. Furthermore, a Setaram Micro DSC was used to measure the heat capacities C_p of different vaterite and calcite samples at room temperature.

Potentiometric measurements of the vaterite–calcite transition

Analytical grade reagents, bidistilled water and pre-humidified high purity (99.995%) CO_2 gas or defined CO_2/N_2 mixtures (1 to 50 vol% CO_2) were employed throughout. Calcite was a commercial product (MERCK p.a.) and used without further purification. Measurements were performed in glass jacketed cells thermostatted at 25.00±0.03°C by a RCS Lauda circulator thermostat. Stirring was provided by a small teflon-coated magnetic stirrer bar. Measurements were terminated when the potentials of the test solutions became constant. The galvanic cells without liquid junction can be represented as:

$$\mathrm{Ag} \mid \mathrm{AgCl} \mid \text{test solution}, I=0.2\ \mathrm{mol\ dm^{-3}\ CaCl_2} \mid \mathrm{GE}$$

where GE is a glass electrode (SCHOTT H2680). Silver–silver chloride reference electrodes of thermal-electrolytic type were home made and employed directly without salt bridge. An Orion pH meter model 940 was used and the potentials were measured to 0.1 mV. Scanning electron microscopy (SEM) was also employed to investigate the transformation of vaterite samples during potentiometric measurements.

The potentiometric method to obtain the Gibbs energy of transition $\Delta_{trs}G^*$ reported by Königsberger *et al.* [16] was adopted in this work. Two measurements were carried out simultaneously but one test solution contained calcite and the other contained vaterite. The background electrolyte was actually a 0.001 mol dm^{-3} HCl/ 0.2 mol dm^{-3} $CaCl_2$ solution; in which both pairs of electrodes were calibrated to an arbitrary value, i.e. the calcite and vaterite cells have the same initial potentials. Each measurement was performed under constant CO_2 partial pressure and 400 mg of either calcite or vaterite were added into 70 ml of the background electrolyte solution. As shown by Königsberger *et al.* [16], the potential difference between the calcite and vaterite cells multiplied by twice the Faraday constant is equal to $\Delta_{trs}G^*$.

Results and discussion

Calorimetric study of the vaterite–calcite transition

The phase transition of vaterite into the stable modification calcite takes place when being thermally activated at temperatures higher than 600 K [10] or in aqueous solutions near room temperature [17]. The phase transition can be represented as

$$\mathrm{CaCO_3(vaterite)} \rightarrow \mathrm{CaCO_3(calcite)} \tag{1}$$

The phase transition enthalpy $\Delta_{trs}H^*$ can be determined using different techniques. Direct measurements of the transition enthalpy can be achieved with vaterite samples either thermally activated at high temperature or in aqueous $CaCO_3$-saturated solution at low temperature. The phase transition enthalpy can also be determined indirectly by the difference between the reaction enthalpies Δ_rH of calcite and vaterite with alkaline EDTA solution respectively. However in the latter method, a proper mathematical description of the calorimetric arrangement on the basis of special calibration experiments is the prerequisite for a reliable evaluation of the long reaction periods of the dissolution measurements. After correction for water content in each vaterite sample used, the results obtained from the calorimetric study of the vaterite–calcite transition are summarised in Table 1. It should be noted that (i) the experimental uncertainty ($\pm b$) given in this work equals twice the standard deviation, i.e. $b=2\sigma$ [18], and (ii) the uncertainty of a derived value is assigned using the statistical procedures outlined in [19].

Table 1 Calorimetric and potentiometric results of the vaterite–calcite transition ($\Delta_{trs}H^*$ values were corrected for water content in each vaterite sample)

Methods	Quantity	$\Delta X\pm 2\sigma$/ kJ mol^{-1}	Number of measurements
Thermally activated (630–770 K)	$\Delta_{trs}H^*$	–3.1±0.2	28
In $CaCO_3$-saturated solution (298–353 K)	$\Delta_{trs}H^*$	–3.4±0.2	14
Vaterite reacted with alkaline EDTA solution (313 K)	$\Delta_rH(V)$	–36.3±0.7	20
Calcite reacted with alkaline EDTA solution (313 K)	$\Delta_rH(C)$ $\Delta_{trs}H^*$	–32.9±0.5 –3.4±0.9	12
Potentiometric study of vaterite A (298.15 K)	$\Delta_{trs}G^*$	–2.9±0.2	17
Potentiometric study of vaterite D (298.15 K)	$\Delta_{trs}G^*$	–3.3±0.4	13

Results of the kinetic investigation of the thermally activated phase transition were given in [10]. From these results it was found that the phase transition temperature T_{trs} strongly depends on sample preparation. Whereas sample A has the highest transition temperature observed at about 725 K, the lowest transition temperature is obtained with sample E at around 630 K. Sample D also gives a low transition temperature (651 K) and an extra endothermic peak is found at an onset temperature of 699 K. This endothermic peak was reported earlier by Rao *et al.* [20] and their vaterite was also precipitated from calcium salt solution with sodium carbonate like our sample D. The variation in transition temperature could be a consequence of minute quantities of some specific chemical impurities [1, 10]. However the discrepancies in the phase transition enthalpies of different vaterite samples are not significant so that the mean value, –3.1±0.2 kJ mol^{-1}, is reported in Table 1.

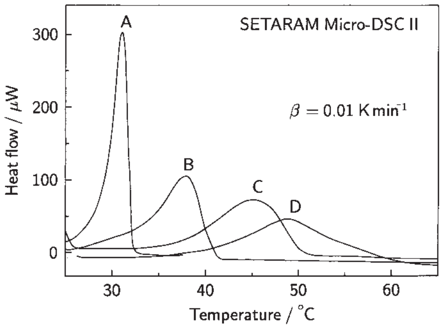

Fig. 1 Non-isothermal study of the vaterite–calcite transition in $CaCO_3$-saturated solution at low temperature for vaterite samples A to D

Results of the non-isothermal measurements in $CaCO_3$-saturated solution at low temperature are also shown in Fig. 1. It can be seen from this figure that the transformation of samples A to E is in reverse order compared with the results obtained from the thermally activated transition at high temperature. More details of the phase transition kinetics are given in [21]. As a consequence of the nearly equal heat capacities of both polymorphs (see results of the entropy determination), the temperature dependence of $\Delta_{trs}H^*$ is negligible and the average of the results obtained in the temperature range 298–353 K, –3.4±0.2 kJ mol^{-1}, is presented in Table 1.

It is obvious from the small experimental uncertainties of the $\Delta_{trs}H^*$ values reported in Table 1 that the sample preparation methods do not exert a strong influence on the results obtained in this work. Overall, the results shown in Table 1 clearly reveal that for the determination of vaterite–calcite transition enthalpy at low temperature, the direct measurement of the transition in $CaCO_3$-saturated solution, –3.4± 0.2 kJ mol^{-1}, is more precise than the indirect method calculated from the difference between the dissolution enthalpies Δ_rH of the two polymorphs, –3.4±0.9 kJ mol^{-1}. However the excellent agreement of the results obtained from the two methods strongly supports the reliability of our results. Our recommended values for $\Delta_{trs}H^*$ is therefore –3.4±0.2 kJ mol^{-1}. It is also noteworthy that, given the experimental uncertainties, no temperature dependence of $\Delta_{trs}H^*$ can be derived even for the range 300 to 725 K.

Potentiometric study of the vaterite–calcite transition

At (metastable) solubility equilibrium, the pH values of the test solutions having the ionic strength I in the two parallel potentiometric cells correspond to the following reactions

$$\mathrm{CaCO_3(calcite\ or\ vaterite)+2H^+(\mathit{I},\ calcite\ or\ vaterite)} \leftrightarrow \mathrm{Ca^{2+}(\mathit{I})+CO_2(g)+H_2O(\mathit{I})} \qquad (2)$$

The difference in the potentials of the cells is directly related to the Gibbs energy of transition of reaction (1). The advantages of the method employed here were discussed in [16]. These include (i) the concentration of $CaCl_2$ and partial pressure of CO_2 are equal in two cells, (ii) Ca^{2+} concentration in the background electrolyte is much higher than that resulting from the solubility difference between vaterite and calcite. Therefore neither Ca^{2+} concentrations nor partial pressures of CO_2 need to be known accurately. Since only the relative quantity is of interest, an absolute value from a proper calibration of the electrodes is not needed. Extrapolation to $I=0$ is also not necessary. Overall just the pH difference between two cells is the relevant quantity.

Vaterite samples A and D were used in the potentiometric study of the vaterite–calcite transition at 25°C. SEM photos of samples taken during measurements and X-ray diffractograms of samples taken before and during experiments show that calcite was the only product of the transformation, i.e. no aragonite was detected. For each type of vaterite samples used, the composition of the gas phase employed (pure CO_2 or CO_2/N_2 mixtures) changes the potentials of the cells but it has no significant effect on the potential difference between the calcite and vaterite cells.

Examples of the potential *vs.* time curves for samples A and D are presented in Fig. 2. The results from 17 pairs of vaterite A – calcite measurements and 13 pairs of vaterite D – calcite measurements are also reported in Table 1. It can be seen clearly from Fig. 2 that vaterite D takes more time for the transformation to calcite than vaterite A; this agrees with the observation of the transition in aqueous $CaCO_3$-saturated solution at low temperature (see above). Also the minimum potential of sample D was found to be more negative than that of A, resulting in a small difference in the $\Delta_{trs}G^*$ values of the two samples so that vaterite A, -2.9 ± 0.2 kJ mol^{-1}, is apparently more stable than D, -3.3 ± 0.4 kJ mol^{-1}. Although the difference in $\Delta_{trs}G^*$ between the two samples is not very large, it is in accord with the variation in the thermally activated transition temperature (discussed above). However, the Na_2CO_3 impurity in vaterite D may actually have caused the metastable equilibrium pH of its solution to be more alkaline than that of sample A so that the more negative $\Delta_{trs}G^*$ of sample D may just be an artefact. Since vaterite A is the purest amongst the samples used, its $\Delta_{trs}G^*$ is therefore chosen to represent the Gibbs energy of transition from vaterite to calcite.

Determination of the heat capacity and the standard entropy of vaterite

Measurements of the heat capacity C_p of the $CaCO_3$ polymorphs calcite and aragonite at different temperatures and determinations of the molar standard entropy S^* are well known from different publications [22–30]. Particularly near room and at lower temperatures the agreement of values from different sources seems to be satisfactory. Heat capacity measurements for both phases were performed in the temperature range from 290 to 355 K. Results for calcite are shown in Table 2 and those for aragonite are given in [31]. The high accuracy of these measurements (uncertainty smaller than 1%) was proved using a reference sample of sapphire.

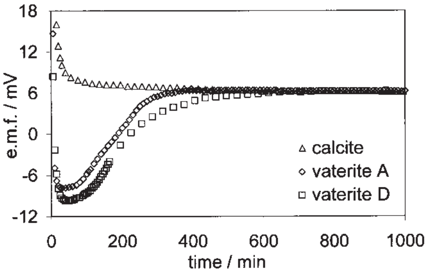

Fig. 2 Typical results of the potentiometric measurements on vaterite samples A and D

In this work, similar measurements were carried out with different vaterite samples. The heat capacities of 17 $CaCO_3$ samples determined at 293 K are given in Fig. 3. Samples 1 to 8 are different vaterites, samples 9 and 10 are calcites from the thermally activated phase transition of vaterites, samples 11 to 15 are calcites from different sources, samples 16 and 17 are aragonites. The higher C_p values of the calcites from vaterite samples compared to the other calcite results may be caused by lattice defects. However the unusually high C_p values obtained from different vaterite samples and the discrepancies amongst them are due to the water content in each sample. After a correction for this, the C_p values for all vaterite samples (shown in Table 2 and Fig. 3) are comparable to the values for calcite and aragonite within the experimental uncertainties. Given the uncertainties in Table 2, the only information which can be derived for the temperature range 293–353 K is $\Delta_{trs}C_p^*=0$.

Table 2 Heat capacity, $(C_p\pm2\sigma)$/J K^{-1} mol^{-1} (after correction for water content in vaterite samples)

Temperature/K	Calcite [31]	Vaterite
293	81.7±0.6	81.4±1.0
313	84.3±0.6	84.8±1.0
333	86.8±0.6	87.8±3.0
353	89.2±0.6	91.5±3.8

From the C_p results discussed above, we concl 00ude that a similar correction should be necessary for the previously reported heat capacities measured at lower temperatures and hence for the standard entropy of vaterite [32]. For the estimation of entropies for solids, the standard entropy S_{298}^*(H_2O, ice-*I*)=44.7 J K^{-1} mol^{-1} for each water of hydration in a crystalline solid hydrate was suggested by Langmuir [33] and later recommended by Grenthe *et al.* [19]. This value was employed in this work for the water correction and the result obtained at 298.15 K for vaterite sample A is S^*=93.6 J K^{-1} mol^{-1} with a probable uncertainty of ±0.5 J K^{-1} mol^{-1}. Using the standard entropy value of calcite 91.7 J K^{-1} mol^{-1} given by Staveley and Linford [22], the resulting $\Delta_{trs}S^*$ is –1.9 J K^{-1} mol^{-1}. It should be noted that completely anhydrous vaterite cannot be produced to date. As mentioned above, thermogravimetric mea-

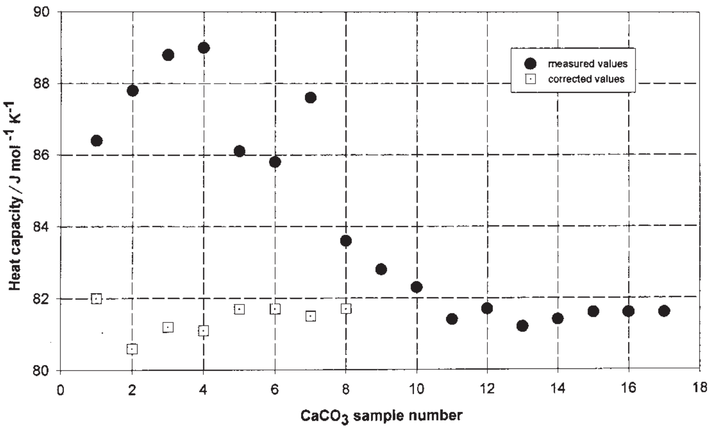

Fig. 3 Heat capacity of different $CaCO_3$ samples. (Samples 1–8: different vaterites, samples 9 and 10: calcites from the thermally activated phase transition of vaterites, samples 11–15: calcites from different sources, samples 16 and 17: aragonites)

surements show that the last quantity of water is released only near the transition temperature. Thus it seems that water traces are needed to stabilise the vaterite structure.

Comparison to the previously reported values

Table 3 summarises the thermodynamic quantities for the vaterite–calcite transition at 298.15 K. On the one hand, a good agreement is obtained for $\Delta_{trs}G^*$ reported by all groups. On the other hand, there is some variation in $\Delta_{trs}H^*$ values determined by each group, and as a consequence, differences are also found for the corresponding $\Delta_{trs}S^*$ values. In general, calorimetrically determined $\Delta_{trs}H^*$ values are more reliable than values derived from the temperature dependence of the corresponding solubility constants like those reported in [34]. Turnbull [1] determined $\Delta_{trs}H^*$ values as –4.33± 0.06 kJ mol^{-1} for a vaterite sample prepared with 30 min precipitation time and between –3.5 and –3.7 kJ mol^{-1} for other vaterites aged longer (up to 2 h in the mother liquor). It should be noted that the uncertainty given by Turnbull (±0.06 kJ mol^{-1}) is rather unrealistic since his reported values for $\Delta_{trs}H^*$ were obtained as the difference between the calorimetrically measured reaction enthalpies of vaterite and calcite with CO_2 saturated 0.1 mol dm^{-3} HCl solution respectively. Although the recommendation by Garvin *et al.* [35], –4.3±1.6 kJ mol^{-1}, seems to be based on Turnbull's value, –4.33 ±0.06 kJ mol^{-1}, our result, –3.4±0.2 kJ mol^{-1}, lies well within the uncertainty given in [35]. Moreover, as pointed out earlier, our $\Delta_{trs}H^*$ value can be regarded as highly reliable because it was obtained from two different experimental techniques. Also the $\Delta_{trs}S^*$ calculated from our $\Delta_{trs}G^*$ and $\Delta_{trs}H^*$, –1.7±0.9 J K^{-1} mol^{-1}, agrees very well with that calculated from the experimentally determined S^* values of vaterite and calcite, –1.9 J K^{-1} mol^{-1}.

Table 3 Thermodynamic quantities for the vaterite–calcite transition at 298.15 K

Quantities	This work[a]	Plummer & Busenberg [34][b, c]	Garvin *et al.* CODATA [35][b, d]	Turnbull [1][b]
$\Delta_{trs}G^*$/kJ mol^{-1}	–2.9±0.2	–3.2± 0.2	–3.3±1.5	–3.3 ±0.1
$\Delta_{trs}H^*$/kJ mol^{-1}	–3.4±0.2	–4.5± 1.8	–4.3±1.6	–4.33±0.06
$\Delta_{trs}S^*$/J K^{-1} mol^{-1}	–1.7±0.9	–4.2±11.8	–3.4±4.2	–3.47

[a] uncertainties given as ±2σ
[b] uncertainties as given in the original papers
[c] [34] calculated all quantities from log*K* (*T*)
[d] [35] compiled from quantities previously reported in literature

Conclusions

In the present paper, the thermodynamic quantities for the vaterite–calcite transition at 298.15 K were carefully determined using different experimental techniques. Although the method to prepare vaterite has some influence on $\Delta_{trs}G^*$ and on the onset temperature of the thermally induced phase transition, the differences in the results obtained from various vaterite samples are not very significant. Unless an improved method to prepare pure anhydrous vaterite is developed (if this is possible at all), the procedure to correct for the water content proposed in this work seems most suitable to obtain the thermodynamic quantities of vaterite. The recommended values are –2.9 ±0.2 kJ mol^{-1}, –3.4±0.2 kJ mol^{-1} and –1.7±0.9 J K^{-1} mol^{-1} for $\Delta_{trs}G^*$, $\Delta_{trs}H^*$ and $\Delta_{trs}S^*$, respectively.

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