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Dedicated to Prof. Antonius Kettrup on the occasion of his 60th birthday

THERMOCHEMICAL INVESTIGATIONS OF CALCIUM CARBONATE PHASE TRANSITIONS

I. Thermal activated vaterite–calcite transition

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Abstract

The vaterite–calcite transition above 630 K has been studied by isothermal and non-isothermal differential scanning calorimetry. Vaterite samples prepared under different conditions were investigated. The transition temperature is strongly dependent on the sample preparation. The observed transition enthalpy ΔH_{tr} is nearly equal for different samples and experimental conditions. From 28 measurements a value of $\Delta H_{tr}= -(3.12\pm0.11)$ kJ mol^{-1} was obtained. The activation energy for the polymorphic transition was calculated from the Arrhenius plot and by use of isoconversional methods, as a function of the degree of conversion. The influence of the kinetic model distortion and experimental uncertainties on the obtained data was discussed. The actual value of the activation energy was assessed at $E_a=(250\pm10)$ kJ mol^{-1} for nearly all examined samples. Functions, corresponded to the model mechanism of nuclei formation and growth, provide the unambiguous consideration of the transition kinetic for the investigated vaterite samples. Differences in the dynamic behaviour of several samples at the transition are established.

Keywords: calcite, kinetic, phase transition, thermal activation, transition enthalpy, vaterite

Introduction

Calcium carbonate occurs in three anhydrous polymorphic modifications, vaterite, aragonite and calcite. Calcite is the most stable phase at room temperature and atmospheric pressure; the least stable one is vaterite. Consequently aragonite and vaterite should transform into calcite. In fact, vaterite is relatively rare in nature and samples prepared in laboratory convert irreversibly in calcite or aragonite in aqueous medium or on heating above 700 K [1–3]. Aragonite transform at atmospheric pressure into calcite under conditions, similar to the vaterite transition [3–6]. However, deposits of aragonite are widespread both in

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the earth's crust and in marine environment; they have persisted for millions of years without any transformation into calcite. The predominance of one polymorph over the others must be considered as a result of kinetic rather than thermodynamic limitations. Thus, a complete understanding of processes occurred at the polymorph transitions in calcium carbonate require knowledge about factors governing the transition kinetic. The dynamic of the transition between different $CaCO_3$ polymorphs has not been well characterised until now.

Further, only for the aragonite–calcite transition high-precision enthalpy values are available [6]. Thermochemical investigations of the vaterite–calcite transition reported so far mostly don't meet the desirable standards of accuracy.

In this study the transition of vaterite into calcite at high temperatures was investigated by means of differential scanning calorimetry (DSC). It was attempted to provide isothermal and non-isothermal DSC data with a precision sufficient for the determination of reliable transition enthalpies and for the estimation of accurate kinetic parameters. The effect of sample preparation on the phase transition was examined. Results of the kinetic analysis of DSC data were compared with those, obtained from X-ray diffraction (XRD) data at different temperatures.

Experimental

Sample preparation

Sample A was prepared by passing a rapid CO_2 stream through a stirred solution containing 180 ml of 1 M $CaCl_2$ and 250 ml of 2 M NH_3 at room temperature. The precipitate was washed with ethanol, filtered and dried 1 h at 85–90°C.

Sample B was prepared similar to sample A, but the solution was adjusted to pH≈10 during the reaction.

Sample C was prepared by slow dropping (0.1 ml per 2–3 s) of 125 ml 1.5 M $CaCl_2$ to 175 ml 2 M K_2CO_3 under stirring at room temperature. After about 40 min the precipitate was washed with water, filtered and dried firstly at room temperature and then 1 h at 70°C.

Sample D was prepared similar to sample C, but $Ca(NO_3)_2$ was used instead of $CaCl_2$.

Sample E was prepared by slow dropping (0.1 ml per s) of 200 ml 1 M $CaCl_2$ to 200 ml 1 M Na_2CO_3 at room temperature. After 30 min (pH≈10.0) the precipitate was rapidly washed with ethanol, filtered and dried at 80°C.

The X-ray diffraction analysis of all samples shows only peaks of vaterite, no other peaks were found. Small amounts of crystal water could not be excluded.

Methods

DSC data were obtained by a Setaram DSC 111 device using CO_2 atmosphere and sample mass 220–260 mg. The first part of the recorded isothermal DSC curves, given by thermal relaxation after drop of the sample into the calorimeter, was reconstructed by use of physically meaningful assumptions. The baseline construction was performed under consideration of a heat capacity change with the reaction progress. The uncertainty of the degree of conversion α ($0\leq\alpha\leq1$) calculated from isothermal and non-isothermal DSC measurements is below 0.02 and 0.01, respectively.

Powder X-ray diffractometry was carried out by uses a STADIP unit from STOE & CIE GmbH and a MZ VI unit from Rich. Seifert & Co. with CuK_α radiation. The degree of conversion was calculated from the integral intensity of vaterite (111) and calcite (104) reflections, calibrated with respect to the pure vaterite and calcite. The uncertainty of the obtained α is at least 0.05.

Kinetic analysis in the solid phase

The consideration of the reaction kinetic in the solid phase and the reliability of the determined kinetic parameters has been subject to much doubt [7–10]. The kinetic for heterogeneous systems was traditionally described by use of equations for homogeneous systems represented in terms of degree of conversion α:

$$d\alpha/dt = k(T)f(\alpha) \tag{1}$$

$$\int_0^\alpha \frac{d\alpha}{f(\alpha)} = g(\alpha) = k(T)\int_0^t dt = k(T)t \tag{2}$$

$$k = E_a/RT \tag{3}$$

The available particular forms of the $f(\alpha)$ and $g(\alpha)$ functions are derived for strongly idealised models concerning the mechanism of the reaction advance in the solid phase. These models are far from the real reaction course [11]. The influence of this discrepancy on the obtained kinetic parameters is unknown; consequently this parameters are mostly physically meaningless. Moreover, the conventional methods of kinetic analysis, based on a model discrimination (selection of $f(\alpha)$ or $g(\alpha)$ form best describing experimental data), deliver ambiguous kinetic information for reactions in solids.

Nevertheless, it is possible to calculate more unambiguous (model-independent) values of the activation energy E_a by means of isoconversional methods. The method suggested by Friedman [12] is based on following relationships, derived from Eqs (1)–(3):

$$\ln\left(\frac{d\alpha}{dt}\right) = -\frac{E_a}{RT} + \ln[Af(\alpha)] \tag{4}$$

$$\ln t=\frac{E_a}{RT}+\ln[g(\alpha)/A] \tag{5}$$

If one consider values of $d\alpha/dt$, T and t, at which in different DSC experiments the same value of α was reached ($\alpha=\alpha_k$ =const), the activation energy can be calculated from the slope of the linear relationships $\ln(d\alpha/dt)_{ik}$ *vs.* $1/T_{ik}$ or $\ln t_{ik}$ *vs.* $1/T_{ik}$. The actual form of $f(\alpha)$ may be unknown, but must be constant for all considered measurements [10]. The Friedman method can be applied both to isothermal and non-isothermal experiments.

Flynn-Wall [13] and Ozawa [14] have proposed a method (so-called FWO method) based on the following equation:

$$\ln\beta=-1.05\frac{E_a}{RT}+\ln\frac{AE_a}{R}-5.33-\ln g(\alpha) \tag{6}$$

For $\alpha=\alpha_k$ =const the plot of $\ln\beta_i$ *vs.* $1/T_{ik}$, obtained from measurements at different heating rates β_i, should be a straight line.

To obtain unambiguous characteristics of the process dynamic in solids, someone may go on according to a scheme, described in [10]. The activation energy can be determined as a function of α by means of the Friedman and FWO methods (Eqs (4)–(6)). In case of the Friedman method the joint treatment of isothermal and non-isothermal measurements is preferred, since by such an analysis temperature lags in the sample become detectable.

Further, the comparison of isothermal measurements at various temperatures, transformed into the coordinate system α *vs.* reduced time [15], seems to be useful. The experimental curves are identical in this coordinate system, if the actual $f(\alpha)$ form is constant with respect to the temperature (for processes with a single rate-limiting step). Differences between curves indicate the dissimilarity of the true $f(\alpha)$ form. Such deviations affect the use of isoconversional methods.

From isothermal measurements a clear value of the activation energy can be determined also by means of the Arrhenius equation (Eq. (3)). The obtained results are independent from the applied kinetic model [16].

The form of $f(\alpha)$, which enable the best description of the experimental data with respect to both the statistical goodness and the provided activation energy value (the deviation from the model independent value of E_a determined above must be as small as possible), could be selected. The chosen function must describe well both the isothermal and non-isothermal data.

According to the proposed procedure a self-consistent set of kinetic parameters can be established. But one must be aware, that there are only optimised data, which clearly characterise the dynamic of the given process. Conclusions about the mechanism, based on the obtained form of $f(\alpha)$, may be done only with special care.

Results and discussion

Differential scanning calorimetry

DSC measurements, performed with linear temperature increase, exhibit for all examined vaterite samples a single exothermic peak above 630 K due to the transition of vaterite into calcite. The transition was confirmed always by XRD investigations. Figure 1 shows the temperature dependence of the heat flow for sample A, observed at different heating rates. The enthalpy of transition is approximately equal for the studied samples, except for sample D (Table 1).

But the temperature of the transition is quite different for the examined vaterite samples. Figure 2 depicts a comparison between the temperature dependencies of the heat flow for several samples (heating rate 5 K min^{-1}). The

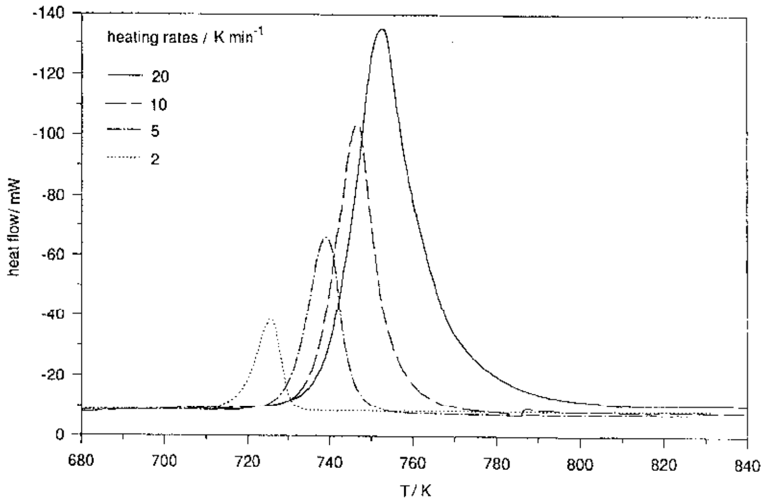

Fig. 1 Temperature dependences of the heat flow obtained for the transition of vaterite sample A at different heating rates

Table 1 Phase transition enthalpy for several vaterite samples (temperature range 630–770 K)

Vaterite sample	$\Delta H^{*}_{\mathrm{tr}}$/kJ mol^{-1}		
	non-isothermal DSC	isothermal DSC	all curves
sample A	–3.07±0.07	–3.09±0.05	–3.08±0.07
sample B	–3.08±0.08	–3.12±0.11	–3.11±0.10
sample C	–3.27±0.09	–2.97±0.10	–3.05±0.13
sample D	–3.43±0.09	–3.34±0.10	–3.36±0.10
sample E	–3.10±0.07	–3.15±0.14	–3.14±0.10

*given limits related to 3–7 DSC experiments in each mode

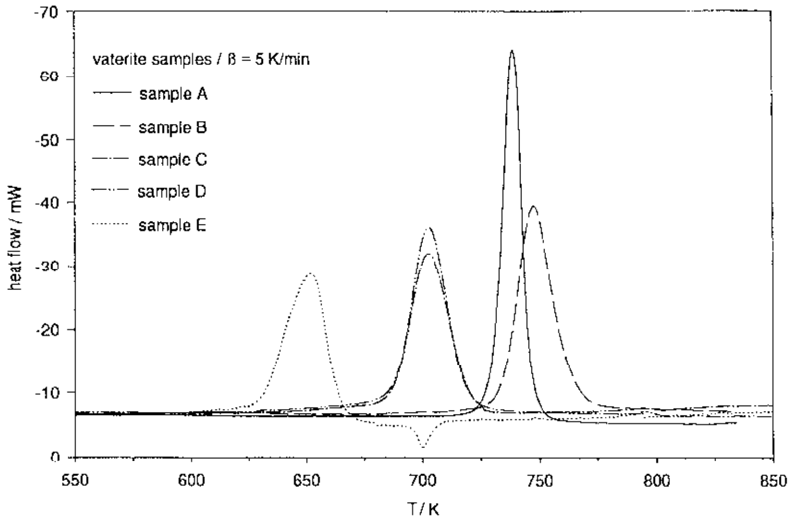

Fig. 2 Measured transition heat flow for several vaterite samples (heating rate 5 K min^{-1})

temperature range, where the vaterite transition proceeds, vary from 630–670 K (sample E) to 730–775 K (sample B). The thermally activated vaterite transition has been obtained earlier only above 700 K [1, 2, 17–19]. The remarkable influence of the sample preparation on the transition temperature could be a consequence of specific chemical impurities occurred in the vaterite sample in very small quantities or may be caused by different contents of amorphous calcium carbonate in the precipitated vaterite [20, 21].

Moreover, isothermal DSC measurements were performed at different temperatures provided well-defined exothermic peaks. The determined values of the transition enthalpy do not depend from temperature and agree well with data, obtained from non-isothermal measurements (Table 1). The mean value of the transition enthalpy resulted from 28 measurements is ΔH_{tr}=–(3.12±0.11) kJ mol^{-1}. Values determined mostly by means of DTA or with low accuracy were reported so far [1, 2, 17–19]. Nevertheless, the value observed by us is in a fairly good agreement with the obtained earlier values of 3.43 kJ mol^{-1} [1] and 3.49 kJ mol^{-1} [17].

Kinetic analysis of the vaterite–calcite transition

Isothermal DSC measurements of the vaterite-calcite transition performed by us at different temperatures were transformed into α *vs.* t_{red} plots, where $t_{red} = t/t_{0.5}$, $t_{0.5}$ denotes the time, required to yield α=0.5 at the given temperature. Figure 3 represents the α *vs.* t_{red} plots for the polymorphic transition of sample A at several temperatures. Plots are non-identical, but the deviations are relatively small. The same was obtained for all other samples. Probably the deviations are consequences of the uncertain calculation of α, caused by problem of the deter-

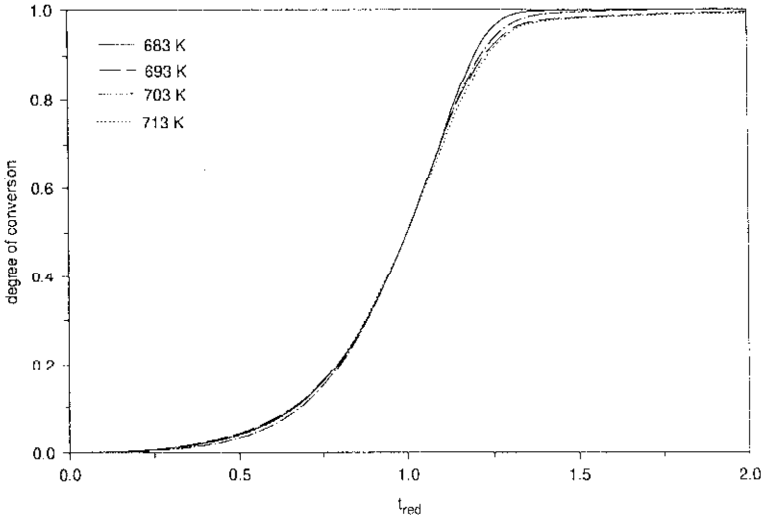

Fig. 3 Degree of conversion *vs.* reduced time plots derived from isothermal DSC curves for the transition of vaterite sample A at given temperatures

mination of the beginning and end of transition or of the baseline construction. But systematical shifts of the plots (and, consequently, of the actual $f(\alpha)$ form) with respect to the temperature were not observed. It can be expected that the activation energy, obtained from isothermal measurements by means of the Friedman method, is only slightly affected by the variations of the $f(\alpha)$ form.

The α *vs.* t_{red} plots obtained for different vaterite samples are not similar (Fig. 4), indicated differences in the actual form of $f(\alpha)$. The function best describing the experimental data has been found for each sample as $n(1-\alpha)[-\ln(1-\alpha)]^{1-1/n}$, but the values of the exponent n are different for various samples (Table 3). This function corresponds to the model mechanism of the formation and growth of product nuclei as a rate-determining step. Values of the activation energy, calculated by means of Eq. (3) for different $f(\alpha)$ forms, were equal. Obtained data are collected in Table 2.

In accordance with the Friedman method transformed DSC data are very well approximated by linear relationships $\ln(d\alpha/dt)_{ik}$ *vs.* $1/T_{ik}$ and $\ln t_{ik}$ *vs.* $1/T_{ik}$ for all examined vaterite samples and α_k values (α_k in the range 0.05–0.95). Figure 5 represents $\ln(d\alpha/dt)_{ik}$ *vs.* $1/T_{ik}$ plots observed for several vaterite samples at α_k=0.5. As can be seen from Figs 4 and 5, considerable differences in the kinetic behaviour are given for different samples.

The data from isothermal and non-isothermal DSC measurements can be described by a common linear relationship (Fig. 5). Therefore temperature lags in the sample should be small and have not a remarkable influence on the determined kinetic parameters [10]. This conclusion is very important due to the large sample mass (more than 220 mg) used.

Table 2 Model independent values of the activation energy for the polymorphic transition of several vaterite samples, calculated according to Eq. (3) and with isoconversional methods, at $\alpha=0.5$

Vaterite sample	E_a^*/kJ mol^{-1}				
	Eq. (3)	Eq. (4) isotherm	Eq. (4) all data	Eq. (5) all data	Eq. (6)
sample A	258	255	255	245	335
sample B	250	275	335	225	400
sample C	254	255	260	220	320
sample D	245	250	270	250	–
sample E	210	200	230	195	–

*the uncertainty of the calculated values is ±5 kJ mol^{-1} by use of Eq. (3) and ±10 kJ mol^{-1} by use of isoconversional methods (considered at $\alpha=0.5$)

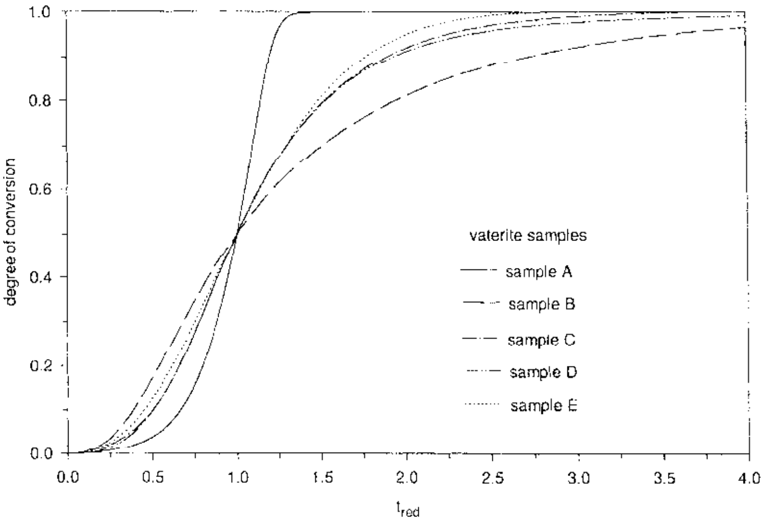

Fig. 4 Degree of conversion *vs.* reduced time plots derived from isothermal DSC curves for several vaterite samples (at given temperatures)

Values received from XRD curves are well described by relationships used for DSC data (Fig. 5). It must be taken into the consideration that the experimental uncertainties of the XRD data are relatively large.

From the slope of the linear relationships between $\ln(d\alpha/dt)_{ik}$ (or $\ln t_{ik}$) and $1/T_{ik}$ the activation energy value can be calculated at various α_k according to the Friedman method. The determined values are model independent. Figure 6 represents the activation energy obtained for sample A as a function of α. The calculated values decrease with increasing α. The difference between E_a determined at

$\alpha=0.2$ and at $\alpha=0.8$ vary from only 40 kJ mol^{-1} for vaterite E to more than 120 kJ mol^{-1} for vaterite B. Differences are much smaller, when Eq. (5) was applied. It is difficult to assess the dependence of the actual value of the activation energy from α, since the calculated E_a value is probably affected by experimental

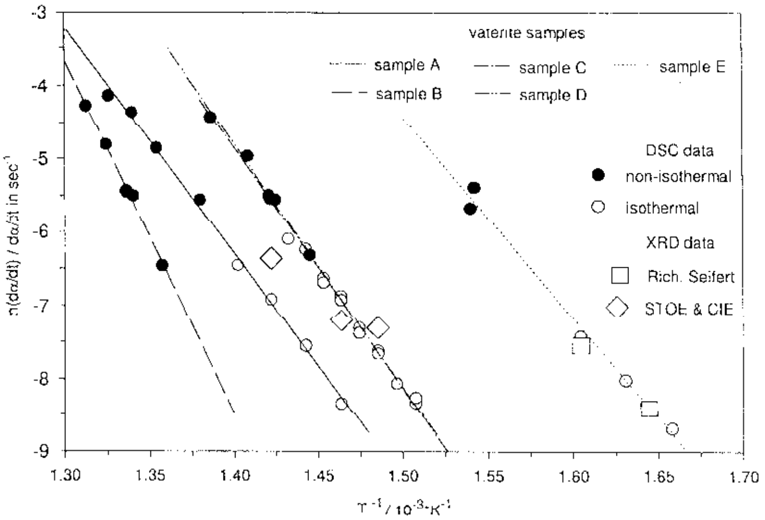

Fig. 5 Isoconversional plots constructed in accordance with the Eq. (4) for several vaterite samples under consideration of isothermal and non-isothermal DSC data and isothermal XRD data, at $\alpha=0.5$

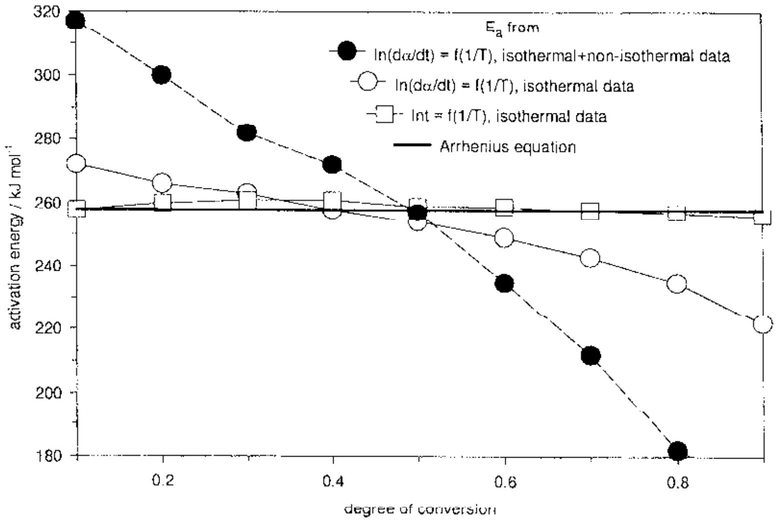

Fig. 6 Activation energy for the transition of the vaterite sample A calculated according to the Arrhenius equation (Eq. (3)) and by use of the Friedman method, as a function of α

Table 3 Values of the exponent n refered to the kinetic function $f(\alpha)=n(1-\alpha)[-\ln(1-\alpha)]^{1-1/n}$ best describing the experimental data according to the proposed procedure

Vaterite sample	Non-isothermal data			Isothermal data
	method [26]	method [23]	method [24]	method [15]
sample A	5.0	–	5.0	5.5
sample B	1.2	–	1.2	1.6
sample C	1.4	–	1.6	1.8
sample D	1.4	–	1.8	2.0
sample E	1.7	1.8	1.7	2.0

uncertainties mentioned above. It is remarkable that at $\alpha=0.5$, where the influence of this uncertainties is much lower, the differences between the activation energy values, calculated by the Friedman method and by the Arrhenius equation, are smaller than 20 kJ mol^{-1} (Table 2).

Activation energy calculated by use of the FWO method is much higher (Table 2). The possible sources of this discrepancy is discussed in [10]. For the assessment of the model independent activation energy only data, obtained by the Friedman method (at $\alpha=0.5$) and with the Arrhenius equation, were taken into the consideration. Despite the differences in the kinetic behaviour of the studied vaterite samples mentioned above, the unambiguous values of the activation energy was found to be approximately the same for nearly all studied samples. The mean value was assessed to $E_a=(250\pm10)$ kJ mol^{-1}. Only for the sample E a value of $E_a=(210\pm10)$ kJ mol^{-1} was found. It should be noted that in [1] for the activation energy of the vaterite–calcite transition a value of 210 kJ mol^{-1} was estimated by use of the Arrhenius equation.

Further, four different methods based on a model discrimination were applied to select the form of $f(\alpha)$, which enable the optimised description of the experimental data. There are linearization methods, proposed by Freeman and Carroll [22], Sharp *et al.* [23], Coats and Redfern [24], as well as the non-linear regression analysis, carried out with the software TA-kin from Anderson [25]. The resulted activation energy values are approximately equal for several methods, but quite different with respect to the applied form of $f(\alpha)$. Functions, provided activation energy values near to the model-independent value given above, were selected. For the Freeman-Carroll method the procedure proposed by Malek [26] was used. The same function, as in case of isothermal data, was found to describe well the non-isothermal data both with respect to the statistical goodness and to the obtained value of the activation energy, namely $n(1-\alpha)[-\ln(1-\alpha)]^{1-1/n}$. The value of the exponent n slightly varies, if measurements with different heating rates were considered. The deviation is larger for sample A, having the fastest transformation from all investigated samples (Fig. 2). Probably, at high heating rates (more than 10 K $\min^{-1}$) temperature lags in the sample appear, which influence the reaction kinetic. At the lower heating rates where such influence is unexpected, the obtained value of n is close to the determined one from isothermal curves. In the Table 3 are given the values of the exponent n, received from measurements with lower heating rates.

Conclusions

The results for the enthalpy change at the vaterite–calcite transition are equal for non-isothermal and isothermal DSC curves approximately and differ slightly with respect to the conditions of the vaterite preparation only. The mean value of the transition enthalpy for several samples was estimated as $\Delta H_{tr}=-(3.12\pm0.11)$ kJ mol^{-1}.

Contrary to the transition enthalpy, the dynamic of the phase transformation is quite different for the studied vaterite samples. The temperature range of the transition varies from 630–670 K for the sample E to 730–775 K for sample B (at heating rate 5 K $\min^{-1}$). The plots $\ln(d\alpha/dt)_{ik}$ *vs.* $1/T_{ik}$ and $\ln t_{ik}$ *vs.* $1/T_{ik}$, constructed in accordance with the Friedman method, also confirm the different dynamic behaviour of the studied samples. At the current degree of conversion α_k a common linear relationship between $\ln(d\alpha/dt)_{ik}$ and $1/T_{ik}$ can be established for data obtained from isothermal and non-isothermal DSC curves and from XRD measurements.

Model-independent values of the activation energy obtained by means of the Friedman method at $\alpha_k=0.5$ and calculated according to the Arrhenius equation are approximately equal. Despite the observed differences in the dynamic behaviour, the activation energy is $E_a=(250\pm10)$ kJ mol^{-1} for all studied samples, except sample E, where $E_a=(210\pm10)$ kJ mol^{-1} was obtained.

The form of $f(\alpha)$, best describing the experimental data, is determined as $n(1-\alpha)[-\ln(1-\alpha)]^{1-1/n}$, corresponded to the model mechanism of the formation and growth of product nuclei. The optimised value of the exponent n for the examined samples seems to be approximately 1.6 ± 0.2 except sample A, where $n\approx5$ was obtained.

The analysis of the kinetic of the phase transition of vaterite into calcite in aqueous medium, as well as of aragonite into calcite both in water and on heating will be the subject of further publications.

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