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Thermochimica Acta 337 (1999) 111–120

thermochimica
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Formal kinetic analysis of processes in the solid state

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Received 18 May 1999; received in revised form 14 July 1999; accepted 16 July 1999

Abstract

The applicability of an unconventional approach in the formal kinetic analysis of solid-state reactions is discussed. This approach is based on the joint use of so-called isoconversional methods and of the non-linear regression analysis. By means of this approach reliable kinetic parameters for the phase transitions between three polymorphic modifications of calcium carbonate were obtained. The influence of the conditions of sample preparation on the transition kinetics has been studied. Two different transition mechanisms are compared using the calculated kinetic data. The isoconversional method, proposed by Friedman, delivers activation energy values, which deviates from data, obtained by means of the Flynn–Wall–Ozawa method. Additionally, the calculated apparent activation energy is dependent on the degree of conversion. The influence of some model deviations on the accuracy of the isoconversional methods is discussed. It is shown that the robustness of these methods towards model deviations may be tested by an analysis of theoretical plots. © 1999 Published by Elsevier Science B.V. All rights reserved.

Keywords: Formal kinetics; Isoconversional methods; Solid state; Phase transition; Calcite

1. Introduction

The determination of reliable kinetic parameters for solid-state reactions is a widely discussed topic. Problems arise from the uncritical use of the general kinetic approach, not taking into account the implemented basic assumptions. It is difficult to express exactly the concentration profile in the solid particle. Simplified models of reactant/product interface movement in hypothetical bodies must be introduced in the kinetic analysis. Thus, the obtained kinetic parameters correspond rather to the chosen idealized model than to the real process. Distortion of the kinetic data due to this discrepancy is normally undefined. Consequently, the available kinetic information is physically meaningless, its applicability to reaction mechanism studies is very doubtful.

From this point of view more attention should be drawn to the formal kinetic analysis. Formal analysis means, that the reaction rate can be expressed as a function of time and temperature using empirical functions. Knowledge of the real reaction mechanism is not essential. Obtained parameters may be useful for various practical applications, e.g. prediction of the reaction progress at different temperature conditions or comparison between reaction kinetics and properties of the solid sample.

Unfortunately, conventional kinetic methods do not permit an unambiguous formal analysis. As a rule, several kinetic models provide a similar statistical

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PII: S0040-6031(99)00242-7

goodness of data approximation, but the corresponding sets of kinetic parameters are quite different [1,2]. For a successful analysis at least one kinetic parameter must be a priori known.

By means of the so-called isoconversional methods the actual value of the activation energy E_a can be determined from multiple runs without knowledge of the true kinetic model. Using the known E_a value, a unique discrimination between the ordinary kinetic models is possible. After the choice of the appropriate model, remaining kinetic parameters can be calculated by means of non-linear regression analysis. This two-part approach is probably the best way for a formal kinetic analysis of processes in solids, because unambiguous kinetic data are obtained.

The aim of this paper is a detailed discussion of two convenient isoconversional methods. We would like to show that the calculation of model-independent values of the activation energy by means of these methods is very useful for a reliable determination of formal kinetic parameters.

Firstly, the basic principles of the isoconversional methods are briefly reviewed. Several conditions for the validity of these methods are specified. The subsequent part of the paper summarizes some of results obtained by the kinetic analysis of the calcium carbonate phase transition according to the mentioned approach. The less stable modifications vaterite and aragonite transform at appropriate conditions into the stable calcite [3–7]. We performed the process monitoring by differential scanning calorimetry (DSC) and X-ray diffraction analysis (XRD). Vaterite and aragonite were prepared by different methods and the influence of the preparation conditions on the transition kinetics has been analyzed. Further, we would like to show that a reliable comparison between two transition mechanisms — in water and on heating — is possible using the calculated formal kinetic parameters. Finally, some considerations, concerning the robustness of the isoconversional methods towards kinetic model distortions, are presented.

2. Experimental

The samples of vaterite were prepared by five different methods. In addition, one synthetic and three natural samples of aragonite were used. Details of the sample preparation were published [6,7]. The phase purity was verified by X-ray diffraction analysis and by chemical analysis.

The thermal activated phase transition was measured by a DSC 111 from Setaram in a CO_2 dynamic atmosphere. Vaterite–calcite transition in water was monitored by a Micro-DSC II from Setaram. Due to the low transition enthalpy a large sample mass (100–300 mg) was necessary to provide the desired data precision. Calcite was used as reference sample. Details were published earlier [6,7].

Powder X-ray diffraction analysis of the phase transitions at higher temperatures was carried out by a STADIP unit from STOE & CIE GmbH and a MZ VI unit from Rich. Seifert & Co. The degree of conversion α was calculated from the integral intensity of the corresponding reflections, calibrated with respect to pure vaterite, aragonite and calcite.

Uncertainties of α, calculated from DSC and XRD data, are roughly 0.02 and 0.03–0.05, respectively.

3. Kinetic approach

Usually, the basic equation of the homogeneous kinetics is applied to the kinetic treatment of solid-state processes:

$$\frac{d\alpha}{dt} = k(T)f(\alpha). \qquad (1)$$

Instead of concentrations the degree of conversion α was used. Assuming the validity of the Arrhenius equation $k = A\exp(-E_a/RT)$, the following rate equations may be written for measurements at a constant heating rate β:

$$\frac{d\alpha}{dt} = A\exp\left(-\frac{E_a}{RT}\right)f(\alpha), \qquad (2)$$

$$g(\alpha) = \frac{AE_a}{\beta R}\exp(-x)\left[\frac{\pi(x)}{x}\right], \qquad (3)$$

where $x = E_a/RT$ is the reduced activation energy and $\pi(x)$ is the temperature integral approximation which has to be introduced because Eq. (2) cannot be solved exactly. The $f(\alpha)$ and $g(\alpha)$ functions are derived on the basis of different models of the reaction interface movement, the corresponding mathematical expressions are well known [8].

Traditionally, the aim of the kinetic analysis of solid-state reactions is the selection of the $f(\alpha)$ or $g(\alpha)$ function, which gives the best approximation of experimental data. The main disadvantage is that several kinetic models provide a similar description of the studied process. This is caused by a strong mutual correlation between the used kinetic functions [1,9]. The choice of the appropriate model on basis of external information (for example from morphological studies) is unreliable due to the discrepancies between the real process and idealized models.

It seems reasonable to determine firstly the model-independent value of the activation energy. An appropriate method is the isoconversional analysis suggested by Friedman [10]. It follows directly from the logarithmized form of Eq. (2):

$$\ln\left(\frac{\mathrm{d}\alpha}{\mathrm{d}t}\right) = -\frac{E_\mathrm{a}}{RT} + \ln[Af(\alpha)], \tag{4}$$

$$\ln t = \frac{E_\mathrm{a}}{RT} - \ln\left(\frac{A}{g(\alpha)}\right). \tag{5}$$

Using data at which in different runs the same value $\alpha = \alpha_k = \mathrm{const}$ was reached, linear relationships $\ln(\mathrm{d}\alpha/\mathrm{d}t)_{ik}$ vs $1/T_{ik}$ and $\ln t_{ik}$ vs $1/T_{ik}$ with a slope proprotional to E_a could be established.

Concerning runs at different heating rates β the method suggested by Flynn–Wall [11] and Ozawa [12] could be applied. From Eq. (3) and the Doyle approximation of the temperature integral [13] follows:

$$\ln\beta = \ln\frac{AE_\mathrm{a}}{R} - 1.052\frac{E_\mathrm{a}}{RT} - 5.33 - \ln g(\alpha). \tag{6}$$

The $\ln\beta_i$ vs $1/T_{ik}$ plot, which corresponds to the chosen value $\alpha = \alpha_k = \mathrm{const}$, should be a straight line with a slope proportional to E_a.

Both isoconversional methods can be applied without knowledge of the true $f(\alpha)$ or $g(\alpha)$ function. But these functions must be invariant for all considered runs. If this basic assumption is not fulfilled, an apparent E_a value would be calculated, which differs from the actual value. The invariance can be examined by comparison of α vs reduced time plots obtained from isothermal runs [14]. For non-isothermal measurements the $y(\alpha)$ and $z(\alpha)$ functions proposed by Malek [15,16] are useful:

$$z(\alpha) = \frac{\mathrm{d}\alpha}{\mathrm{d}t}\pi(x)\frac{T}{\beta}, \tag{7}$$

$$y(\alpha) = \frac{\mathrm{d}\alpha}{\mathrm{d}t}\exp(x). \tag{8}$$

For a single-step process with an invariant $f(\alpha)$ expression, normalized $y(\alpha)$ and $z(\alpha)$ plots as well as α–t_red — plots are independent of the heating rate (non-isothermal runs) and temperature (isothermal runs).

Eqs. (1)–(6) were derived only for the description of single-step reactions. The application of these equations to multiple-step reactions leads to an apparent activation energy value which is influenced by all reaction steps and changes with respect to α [17]. It is preferable to perform the isoconversional analysis at different α_k in order to prove the invariance of the apparent E_a value. Normally, a constant E_a value is assumed in case of single-step reactions.

The calculated model-independent value of the activation energy delivers an unambiguous choice of the appropriate kinetic model. A non-linear regression analysis with a fixed activation energy value or an analysis using the $y(\alpha)$ and $z(\alpha)$ functions [15] are suitable.

4. Results and discussion

4.1. Thermal activated calcium carbonate phase transition

Two modifications of calcium carbonate — vaterite and aragonite — transform into the more stable calcite on heating above 600 K. A single DSC peak can be obtained, which clearly corresponds to the phase transition. The transition of vaterite is exothermic, transition of aragonite is endothermic. It was shown that the transition temperature of vaterite strongly varies with respect to the sample preparation [7]. Consequently, significant differences in the transition kinetics are expected. Formal kinetic analysis would be useful to quantify these differences.

According to the Friedman method, linear relationships $\ln(\mathrm{d}\alpha/\mathrm{d}t)_{ik}$ vs $1/T_{ik}$ were established. They describe well data from isothermal and non-isothermal DSC measurements in the α_k range 0.05–0.95. Further, data from isothermal XRD analysis could be approximated by corresponding relationships. Fig. 1 represents plots obtained for different vaterite and aragonite samples at $\alpha_k = 0.5$.

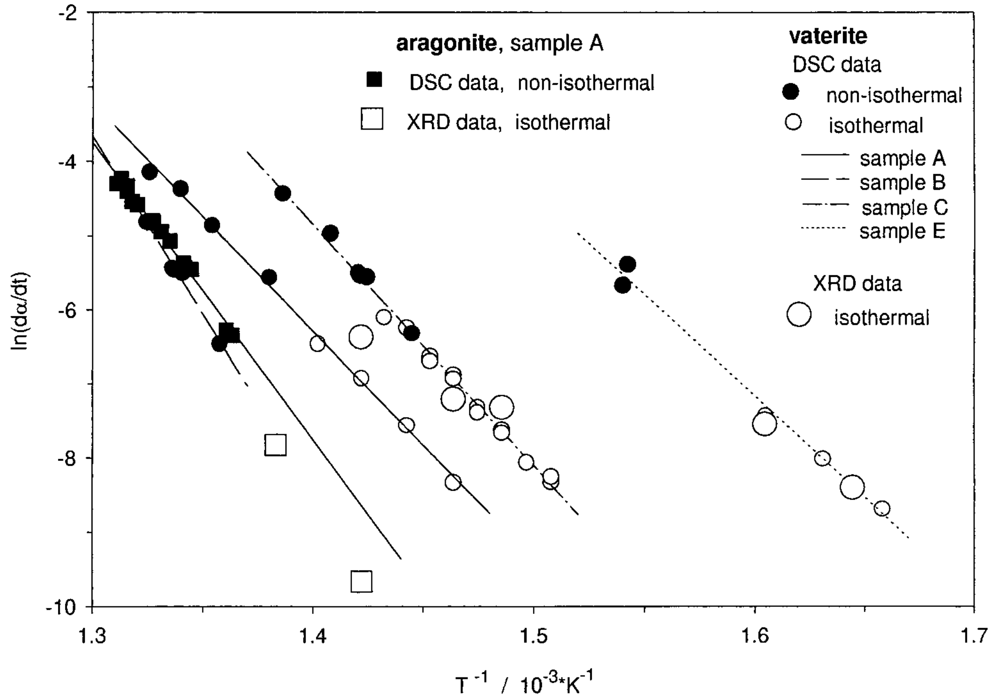

Fig. 1. Transformed DSC and XRD data for the thermal activated phase transition of different vaterite samples and of aragonite into calcite. The points were calculated by the Friedman method (Eq. (4)) from isothermal and non-isothermal runs at $\alpha = 0.5$. The values of $d\alpha/dt$ are given in s^{-1}.

Since common relationships for isothermal and non-isothermal data are obtained, it seems that temperature gradients in the sample are too small to influence significantly the kinetic analysis. It is obvious that such gradients, if they occur, must be much greater in the case of non-isothermal measurements. But we do not observe statistically significant deviations of points, which correspond to non-isothermal measurements. This is a very useful conclusion provided by the Friedman analysis. It should be noted that measurements with variant sample mass do not deliver a reliable result. The reduction of the sample mass leads to significantly greater experimental uncertainties due to the very low reaction heat flow.

Apparent values of the activation energy were calculated by means of the Friedman method, the FWO method as well as by the Arrhenius equation, which also provides model-independent E_a values [9]. Fig. 2 shows results obtained for vaterite samples A and C at different α values. In most considered cases the activation energy is strongly dependent on α. Additionally, several methods give quite different results (Fig. 2).

Earlier it was pointed out that the application of the isoconversional methods to multiple-step reactions leads to a variable activation energy [17]. However, variations, represented in Fig. 2, could not be explained by a multiple-step reaction mechanism. Both the vaterite–calcite and the aragonite–calcite transitions have only one rate-limiting step. This was verified by the simultaneous monitoring of the vaterite (or aragonite) and calcite content by means of XRD. It seems that the basic kinetic assumption about the invariance of E_a with respect to α (for an elementary reaction step) is not always fulfilled for solid-state processes.

The other basic assumption — invariance of the actual $f(\alpha)$ function — is possibly also not fulfilled. For example this could be pointed out by the fact that the $y(\alpha)$ functions, which are shown in Fig. 3 for the vaterite samples A and C, depend on heating rate and temperature (if converted from isothermal data). The $z(\alpha)$ functions and the α–t_{red} – plots also vary from run

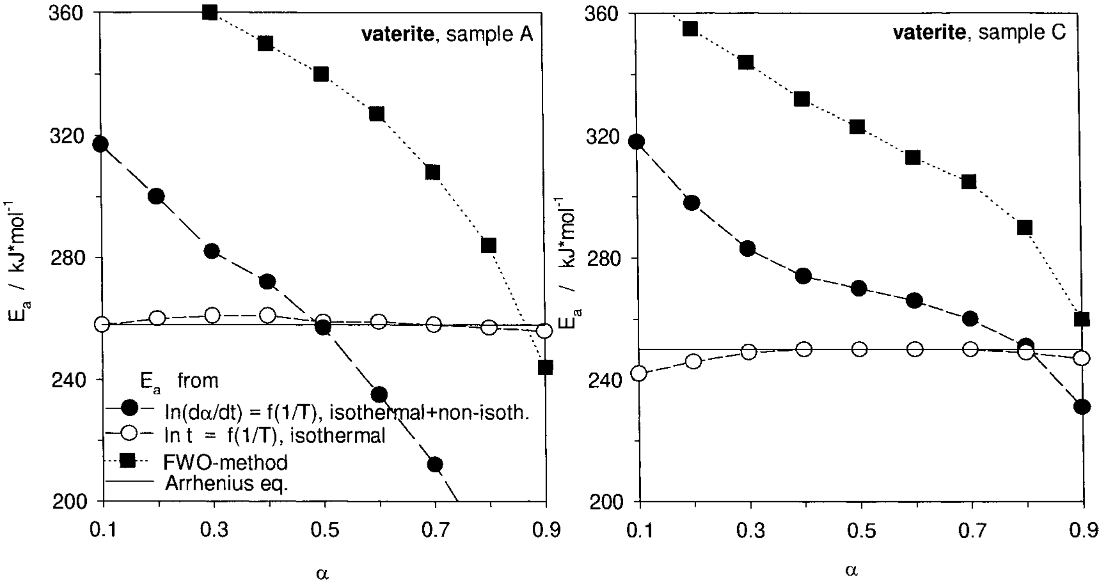

Fig. 2. Model-independent values of the activation energy as a function of the degree of conversion for the thermal activated transition of two vaterite samples into calcite calculated by isoconversional methods and by the Arrhenius equation.

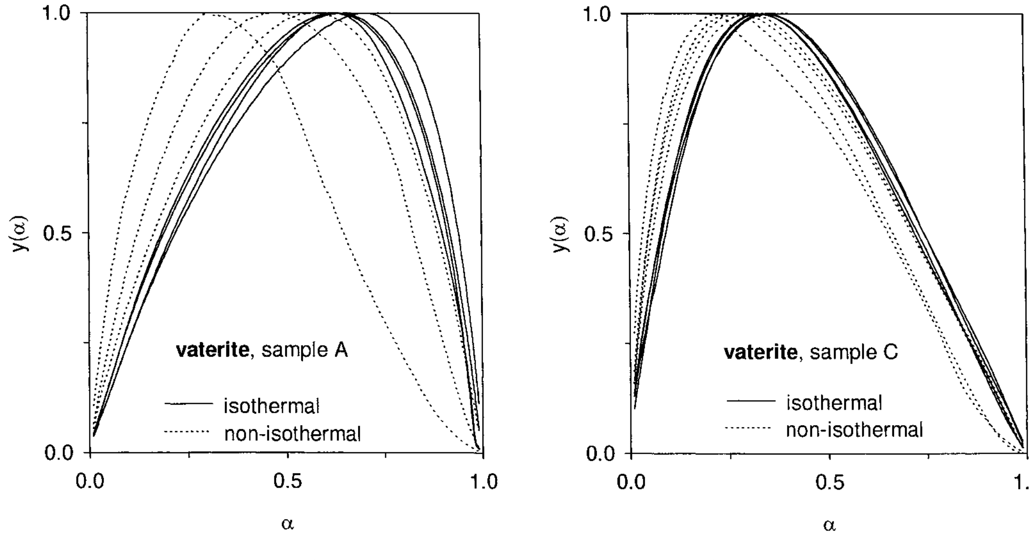

Fig. 3. Normalized $y(\alpha)$ functions calculated from isothermal and non-isothermal DSC data for the thermal activated transition of two vaterite samples into calcite.

to run. But it is necessary to take into account, that variations in the $y(\alpha)$ or $z(\alpha)$ functions also may be caused by the false (constant) E_a value, using for calculations.

Despite the obtained irregularities, the results of the isoconversional treatment allow an unambiguous kinetic analysis according to the two-step approach discussed above. It should be noted that the activation energy values, which was obtained by means of conventional kinetic methods (e.g. non-linear regression analysis), vary in the range 200–1500 kJ mol^{-1} with respect to the applied kinetic model. Results of the

Table 1
Model-independent values of the activation energy and the formal kinetic model for the phase transition of different vaterite samples and of aragonite into calcite in the solid state (thermal activated transition) and in water

Sample	Thermal activated transition		Transition in water	
	E_a (kJ mol^{-1})	Kinetic model	E_a (kJ mol^{-1})	Kinetic model
Vaterite A	250	JMA 5.0	40	JMA 6.0
Vaterite B	270	JMA 1.4	35	JMA 4.5
Vaterite C	260	JMA 1.6	30	JMA 3.5
Vaterite D	260	JMA 1.8	30	JMA 3.5
Vaterite E	210	JMA 1.8	30	JMA 3.5
Aragonite A	370	JMA 2.0	–	–

kinetic analysis, performed with some necessary simplifications, are represented in Table 1.

4.2. Calcium carbonate phase transition in water

In water vaterite transforms into calcite below 360 K [3,18]. A clear, single DSC peak can be observed, which provides a reliable process monitoring. Our investigations point out a variation of the transition temperature with respect to the sample preparation. Thus, the process kinetics depends on the sample preparation. A similar behavior was observed in case of the thermal activated transition. Kinetic parameters, calculated by means of a formal analysis, may be useful for a comparison between various samples and transition mechanisms.

Values, converted from isothermal and non-isothermal DSC data, can be approximated by common linear relationships $\ln(d\alpha/dt)_{ik}$ vs $1/T_{ik}$, shown in Fig. 4. According to the Friedman method, model-indepen-

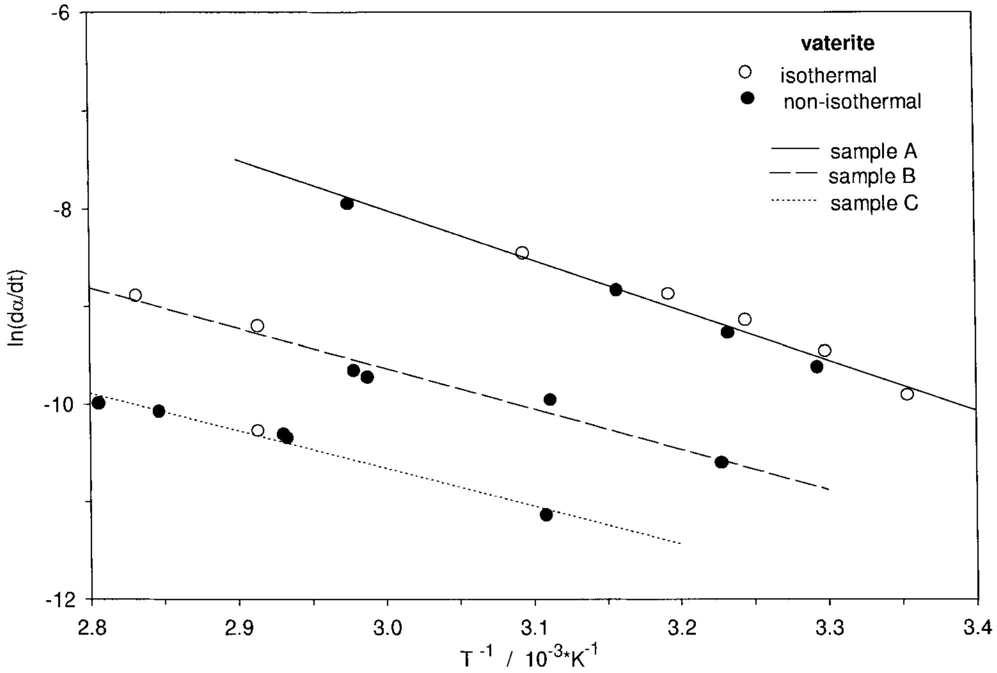

Fig. 4. Transformed DSC data for the transition of different vaterite samples into calcite in water. The points were calculated by the Friedman method (Eq. (4)) from isothermal and non-isothermal runs at $\alpha = 0.5$. The values of $d\alpha/dt$ are given in s^{-1}.

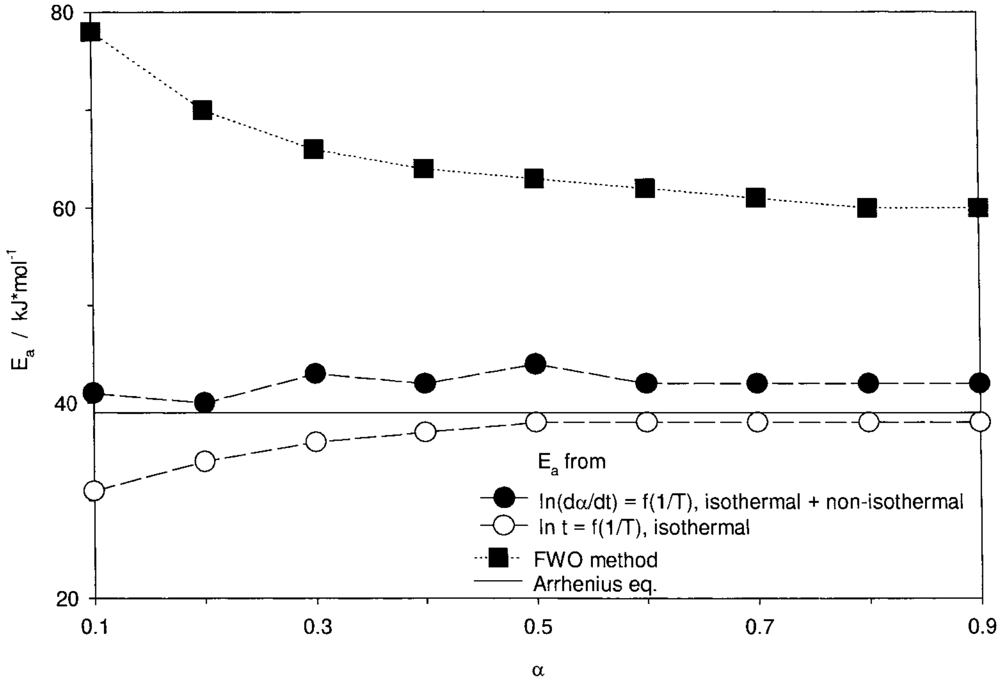

Fig. 5. Model-independent values of the activation energy as a function of the degree of conversion for the transition of vaterite sample A into calcite in water. The points were calculated by isoconversional methods and by the Arrhenius equation.

dent values of the activation energy were determined from the slope of the resulted plots. Obtained values are invariant with respect to α (see Fig. 5). Values of the activation energy were also calculated by means of the FWO method, corresponding data are shown in Fig. 5. The obtained apparent activation energy clearly depends on α. Further, the FWO analysis gives results that are considerable higher than data from Friedman analysis.

Regardless of the disagreement between the results of these two isoconversional methods, a clear discrimination between the usual kinetic models is possible using an approximated model-independent E_a value. The determination of the activation energy by nonlinear regression analysis provides values, which vary in the range 10–500 kJ mol^{-1} with respect to the applied kinetic model.

In Table 1 results of the formal kinetic analysis of the transition of vaterite and aragonite into calcite are compared. The model-independent value of the activation energy is nearly invariant with respect to the sample preparation. This conclusion is valid both for the transition in water and for the thermal activated transition. The invariance of the activation energy is quite remarkable, taking into consideration the mentioned differences between the transition temperature (and, consequently, between the transition kinetics). The activation energy for the vaterite–calcite transition in water, assessed as 30–40 kJ mol^{-1}, is much smaller than values, which were calculated for the thermal activated transition of vaterite into calcite (210–270 kJ mol^{-1}).

In all considered cases the Johnson–Mehl–Avrami (JMA) model [19] with a formal, non-integer kinetic exponent n is the most appropriate. Using this model, the best description of the experimental data was provided both with respect to the statistical goodness of data approximation and to the known value of the activation energy (calculated by means of the isoconversional analysis). The resulted values of the kinetic exponent n are represented in Table 1. Obtained for different vaterite sample values are close together, except sample A. It is of interest that small differences are obtained between the formal kinetic model for the transition in the solid state and in water (see Table 1). The same conclusion follows from the comparison of

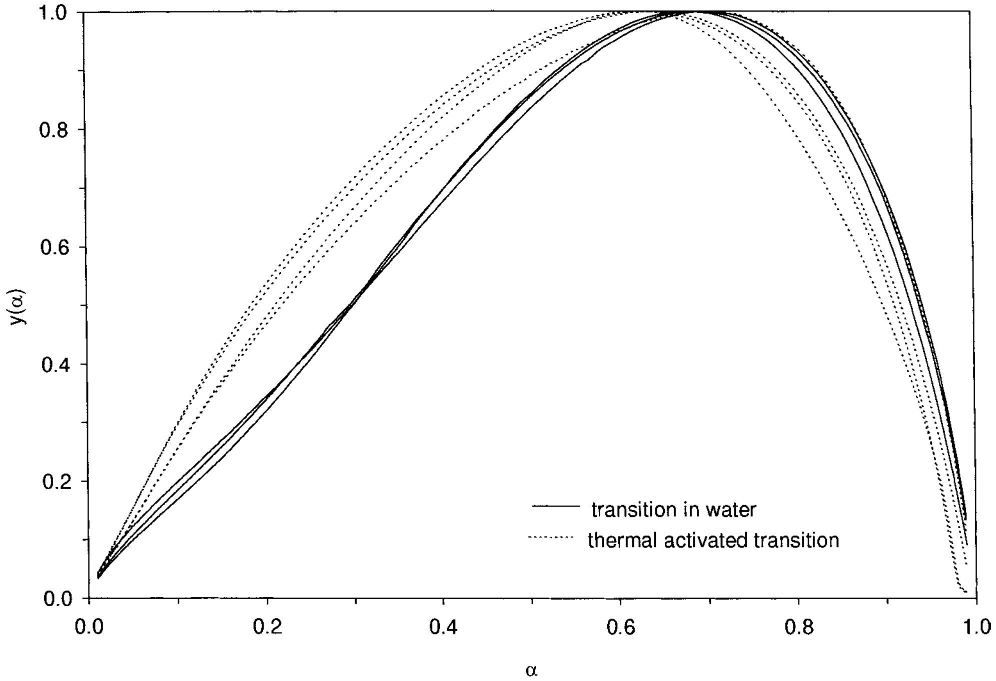

Fig. 6. Normalized $y(\alpha)$ functions calculated from isothermal DSC data for the transition of vaterite sample A into calcite in the solid state (thermal activated transition) and in water.

normalized $y(\alpha)$ functions, as can be seen in Fig. 6 for vaterite sample A. It is known that the $y(\alpha)$ function reproduce the shape of the $f(\alpha)$ function [15].

4.3. Kinetic analysis of theoretical curves

For a better understanding of the observed irregularities, it is useful to investigate the influence of possible model deviations on the accuracy of several isoconversional methods. An analysis of theoretical plots, constructed by means of known parameters, is convenient. The kinetic treatment of theoretical plots shows differences between the recalculated and initial kinetic parameters, if any model deviation occurs during the curve construction. In this manner the robustness of isoconversional methods towards various model deviations may be analyzed. Then it is possible to conclude, which methods are more reliable.

Simulations show that even small variations in the $f(\alpha)$ function from run to run have a significant influence on the activation energy values, calculated both by means of the Friedman and the FWO methods. Additionally, a dependence of the recalculated E_a value with respect to α is obtained.

The robustness of the isoconversional methods towards deviations from the other basic kinetic assumption — invariance of E_a with respect to α — differs significantly. Fig. 7 represents data recalculated from theoretical plots, which are constructed according to the JMA model ($n = 3$) with an activation energy that vary linearly with respect to α from 250 to 200 kJ mol^{-1}. The values of the activation energy estimated using Eq. (4) agree with the initial data. But the activation energy values recalculated using Eq. (5) and the FWO method differ strongly from the initial values.

5. Conclusions

Model-independent values of the activation energy were calculated for the transition of vaterite and aragonite into calcite using two isoconversional methods suggested by Friedman and by Flynn–Wall–Ozawa. It was found that the calculated apparent

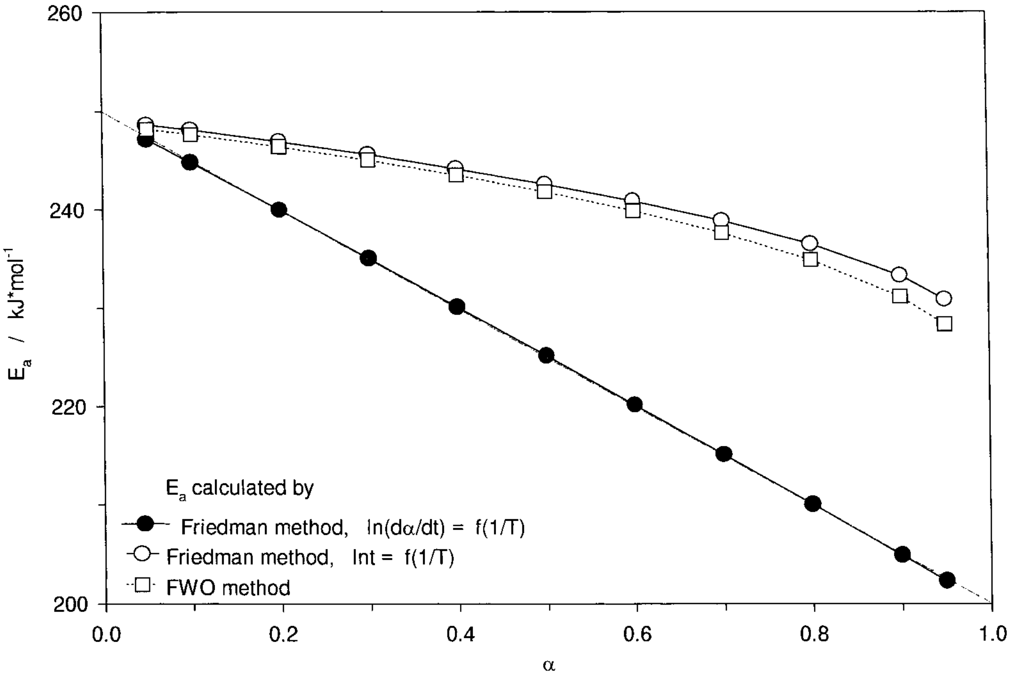

Fig. 7. The values of the activation energy as a function of the degree of conversion calculated from an analysis of theoretical plots by isoconversional methods. The thin dashed line shows the linearly varied E_a value used for the construction of theoretical plots.

activation energy usually depends on α. Despite this irregularity and some differences between the results, obtained by both isoconversional methods, a certain value of the activation energy could be estimated. The known model-independent value of the activation energy permits the unambiguous determination of the appropriate kinetic model and a reliable formal kinetic treatment of the investigated process using the conventional non-linear regression analysis.

It was shown that the determined kinetic parameters allows a meaningful comparison between the transition in water and in the thermal activated solid state as well as between samples, prepared at different conditions. It is remarkable that the calculated activation energy only slightly depends on the sample preparation conditions, although strong differences in the transition temperature and, consequently, in the transition kinetics were obtained.

Analysis of simulated plots shows that the results of the considered isoconversional methods are strongly distorted, if the basic assumption, regarding the invariance of the kinetic model from run to run, is not fulfilled. If the activation energy varies with respect to α, only the Friedman method gives results that agree with initial data, used for the calculation of the theoretical plots.

Acknowledgements

Authors would like to thank Dr. M. Ermrich from STOE & CIE GmbH and Dr. H. Miersch from Rich. Seifert & Co for the XRD investigations. This work was partially supported by the Deutsche Forschungsgemeinschaft.

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