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THE APPLICABILITY OF DTA AND DSC TECHNIQUES TO THE STUDY OF THE KINETICS OF PHASE TRANSITION REACTIONS

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Differential thermal analysis and differential scanning calorimetry techniques have been used to study the kinetics of phase transitions. The aragonite/calcite transformation was chosen as test reaction.

Marked discrepancies were observed between the DTA kinetic results and those obtained from isothermal kinetic measurements. This disagreement is associated with the difficulty of determining accurately the reaction rate of the process from a DTA curve.

In contrast, in DSC measurements, where the reaction rate is given by the height of the peak from the base-line, it is possible to get a satisfactory fit of the data, and the kinetic results obtained with this technique are in good agreement with the isothermal ones.

The valuation of kinetic parameters of phase transitions and crystallization processes from DTA curves has received the attention of many investigators in recent years. In this respect, mention should be made of the new interest shown by Marotta *et al.* [1–4] and other authors [5–8] in the applicability of the Piloyan [9] and Kissinger [10] methods to the analysis of the kinetics of these reactions.

On the other hand, in a recent review on polymorphic transition kinetics by DTA, Dollimore *et al.* [11] point out that DTA "offers a suitable method of determining the mechanism of a reaction which does not involve a weight change or change in physical state-parameters that afford the classical isothermal approach of determining reaction kinetics".

The aim of the present paper is to deepen the knowledge of the application of DTA to study phase transition mechanisms, and also to explore the usefulness of DSC technique for the kinetic study of such reactions.

The aragonite/calcite transformation was chosen as the test reaction. In order to obtain reliable kinetic data on the transformation for comparison with kinetic parameters obtained with these techniques, kinetic analysis of the aragonite → calcite (A → C) transformation was also carried out under isothermal conditions.

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Experimental

Pure synthetic aragonite was prepared following Rao *et al.*'s method [12], by dissolving calcium carbonate (Merck) in an aqueous solution of trichloroacetic acid (Merck). The sample was passed through a 60 μm sieve and analyzed for polymorph purity by X-ray diffraction. No line of the calcite phase was found.

For isothermal runs, samples of aragonite (ca. 50 mg) were deposited in a pyrex holder with iron-constantan thermocouples placed inside the sample, using a tubular furnace situated horizontally. Temperature was recorded using a Fluka 8050 A digital multimeter with an accuracy of $\pm 1°$.

Analysis for aragonite and calcite was carried out by I. R. spectroscopy following the method developed by Rao *et al.* [13]. I. R. spectra were recorded using a Beckman Acculab spectrophotometer.

The DTA patterns were recorded on a Stanton Redcroft model 673-4 instrument, with heating rates in the range of 5 to 20°/min. Calcined alumina was used as the reference material.

DSC curves were obtained with a Mettler TA 3000 instrument, equipped with a TC 10 TA processor unit for evaluating and analyzing the thermal data. An empty aluminium sample pan was used as reference material. A heating rate of 10°/min was employed.

The melting constants of indium were used as standards in the DSC experiments, with the following results: melting point $156 \pm 0.1°$; enthalpy of fusion 292 ± 0.1 J/g; both in good agreement with those reported elsewhere [14].

Results and discussion

The extent of the A → C transformation as a function of time under isothermal conditions is shown in Fig. 1. If compared with the results of Rao [15] for this same material, two main differences are observed in the isotherms in Fig. 1. First, the plots in this Figure are not *s*-shaped, and therefore, the nucleation period is nearly eliminated. Secondly, a clear increase in the rate of transformation exists.

In our opinion, the size of the aragonite particles might account for this different behaviour. As mentioned above, our aragonite sample was sieved and, according to scanning electron micrographs, the needle-like particles were less than 40 μm in length. In Rao's paper [15], no control on the particle size is mentioned and the particles of aragonite studied by this author may well have been larger than those examined in the present investigation.

The kinetic data in Fig. 1 were analyzed with the help of Avrami's and phase boundary equations, generally used to describe the kinetics of phase transition [16]. The integral and differential functions of these equations, $g(\alpha)$ and $f(\alpha)$, respectively, are listed in Table 1.

Plotting of $g(\alpha)$ against time did not reveal the most suitable mechanism from among those included in Table 1 for description of the kinetics of the A → C

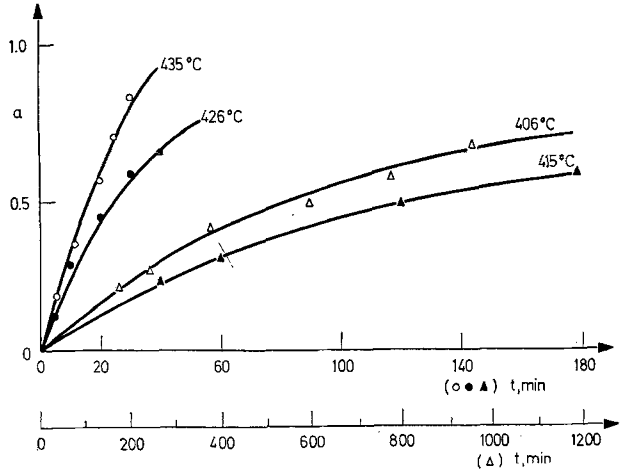

Fig. 1. Extent of reaction (α) of the aragonite/calcite transformation as a function of time at different temperatures

Table 1

Algebraic expressions of differential, f(α), and integral, g(α), functions for the most common mechanisms operating in phase transformations

Symbol	f(α)	g(α)	Denomination
F_1	$(1-\alpha)$	$-\ln(1-\alpha)$	Random nucleation. Unimolecular decay law
A_2	$2[-\ln(1-\alpha)]^{1/2}(1-\alpha)$	$[-\ln(1-\alpha)]^{1/2}$	Random nucleation. Two-dimensional growth of nuclei. Avrami equation
A_3	$3[-\ln(1-\alpha)]^{2/3}(1-\alpha)$	$[-\ln(1-\alpha)]^{1/3}$	Random nucleation. Three-dimensional growth of nuclei. Avrami equation
R_2	$(1-\alpha)^{1/2}$	$2[1-(1-\alpha)^{1/2}]$	Phase boundary controlled reaction for disc.
R_3	$(1-\alpha)^{2/3}$	$3[1-(1-\alpha)^{1/3}]$	Phase boundary controlled reaction for sphere.

phase transition. For the five mechanisms used, moderately acceptable, similar correlation coefficients were obtained. Better results are yielded from the Arrhenius plots included in Fig. 2, where the unimolecular decay law (F_1) gives the best correlation coefficient (0.994).

To overcome the above difficulties, the Sharp and Handcock method [17] was applied to the isothermal curves in Fig. 1. The plots of ln $[-\ln(1-\alpha)]$ *vs.* ln t are

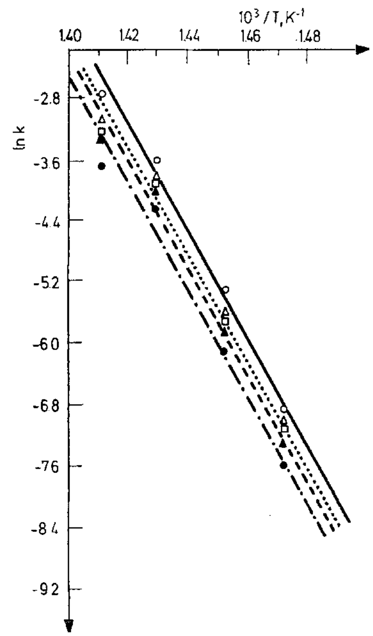

Fig. 2. Arrhenius plots for aragonite/calcite transformation using the kinetic laws listed in Table 1. ○ F_1, □ R_2, △ R_3, ▲ A_2, ■ A_3

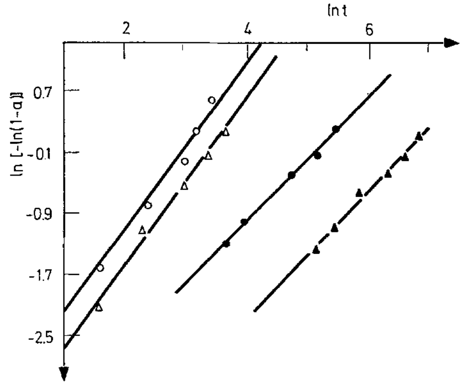

Fig. 3. Plots of ln [$-$ ln (1 $-$ α)] *vs.* ln (time) for aragonite/calcite transformation. ○ 435 °C, △ 426 °C, ● 415 °C, ▲ 406 °C

shown in Fig. 3. The slopes m of the straight lines vary from 1.18 to 0.83 and an average value of 0.98 is obtained, in agreement with $m = 1$ as predicted by the unimolecular decay law (F_1) in Table 1.

The above results seem to indicate that the kinetics of the transformation follow a first-order rate equation, based upon a random nucleation and fast growth of nuclei, similarly to the conclusions reported by Chaudron [18], although this author uses volume changes as an index of the extent of the transformation.

However, our results differ from the data of Rao [15], who finds for *m* values ranging from 1.33 to 1.35. Owing to the scattering observed in the plots of $\ln [-\ln(1-\alpha)]$ *vs.* $\ln t$ for Rao's results [15] (Fig. 6 of the original paper), we have recalculated the values of the parameter *m* from the data in Rao's paper [15] by a linear regression method. The slopes now found disagree with the values reported by Rao, ranging from 1.58 for the isotherm at 440° to 1.29 for the isotherm at 430°, with an average value of 1.40. On the other hand, the explanation given by Rao [15] to justify the fractional value of *m*, based on a possible variation of the surface area of the aragonite during transformation, must be taken cautiously, since our own results [19] do not show any evidence of a change in the particle size of the aragonite.

The activation energy for the transformation, calculated from the slope of the Arrhenius plot in Fig. 2 according to unimolecular decay law kinetics, was 566 ± 40 kJ/mole, slightly larger than the values reported in the literature [16, 20].

The DTA and DSC curves of aragonite show, as expected, a small endothermic effect (Fig. 4; cf. scales in this Figure). Magnification of the DSC curve was carried out by the TC 10 TA processor unit, while in the case of the DTA curve it was done photographically.

The small displacement of the peak temperature in DTA towards higher temperatures (485° in DTA against 477° in the DSC curve) could be ascribed, among others, to the higher heating rate used in the DTA experiment. It is worthy of

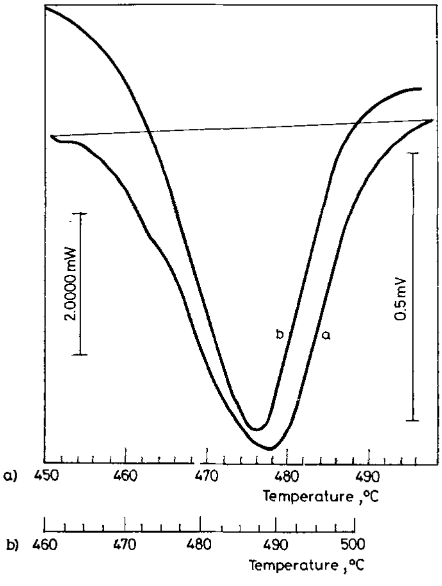

Fig. 4. Thermal curves of aragonite, (a) DSC curve, $\beta = 10°/\text{min}$, (b) DTA, $\beta = 13°/\text{min}$

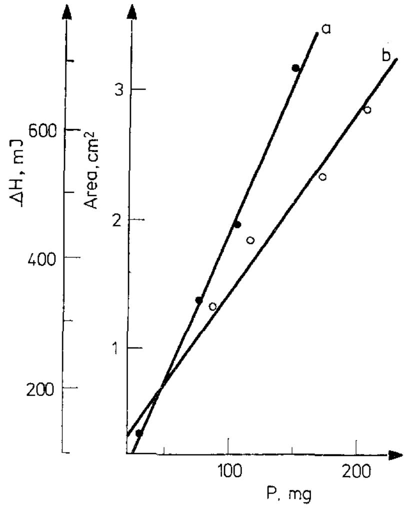

Fig. 5. Effect of sample weight on the aragonite DSC and DTA curves (a) Correlation coefficient 0.997, (b) correlation coefficient 0.989, ● DSC, ○ DTA

note that the value obtained for the aragonite to calcite transition temperature (485°) is markedly larger than the value of 386° reported by Dollimore *et al.* [11]. On the other hand, a good correlation between sample weight and peak area is observed (Fig. 5), although, as expected, the DSC technique provides more quantitative results.

The heat of transformation, ΔH, evaluated from the DSC curves was found to be 4.3 ± 4% J/g. Values between 1.6 and 6.6 J/g have been reported in the literature [21], although values as high as 20 J/g have been calculated from heat capacity data [22].

In recent years, the valuation of kinetic data of devitrification processes and phase transitions from DTA curves has received extensive attention. Marotta and Buri [1–4] have repeatedly proposed two equations for reactions which fit a Johnson–Mehl–Avrami mechanism:

$$\ln \beta = \frac{E}{RT_m} + \text{const.} \qquad (1)$$

and

$$\ln \Delta T = \frac{E'}{RT_m} + \text{const.}, \qquad (2)$$

where β is the heating rate, T_m the peak temperature of the DTA curve, E the activation energy and $E' = nE$, where n is a constant related to the growth of nuclei. Recently, Criado [23] has stated that E and E' are identical parameters. Actually, Eqs (1) and (2) are based upon the Kissinger [10] and Piloyan [9] assumptions, respectively.

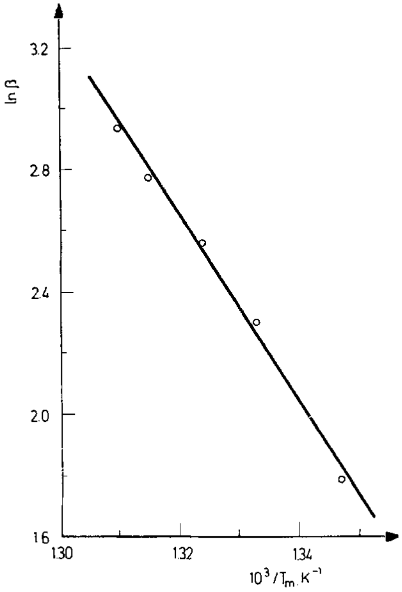

Fig. 6. Plot of ln β *vs.* $1/T_m$. (The values of the peak temperatures T_m have been taken from DTA curves recorded at different heating rates.)

The plot of ln β *vs.* $1/T_m$ for the A → C transformation is shown in Fig. 6. Although a straight line is obtained (correlation coefficient 0.995), the value of the activation energy calculated from the slope, 250 kJ/mole, seems unlikely on the basis of the isothermal kinetic analysis carried out above.

Equation (2) can be deduced from the expression

$$-\frac{d\alpha}{dT} = \frac{A}{\beta}\exp(-E/RT)f(\alpha) \tag{3}$$

following the assumptions of Piloyan [9] and Šestak [24], who consider the reaction rate $d\alpha/dT$ to be proportional to the temperature deflection, ΔT, and that the increase in temperature has a much larger effect on the change in ΔT than on the change in $f(\alpha)$.

Values of ln ΔT, corresponding to α ranging from 0.05 to 0.7 and taken from curve *b* in Fig. 4, are plotted against $1/T$ in Fig. 7, which clearly demonstrates the lack of fitting of the data to Eq. (2) (correlation coefficient 0.962). Similar results were obtained in the analysis of a DTA curve corresponding to the $\alpha \to \beta$ quartz phase transition [25]. Thus, the results described do not support the validity of the application of Piloyan's method of determination of the kinetic parameters of phase transitions from DTA curves.

If the assumption of constant ln $f(\alpha)$ throughout the reaction is rejected, the activation energy of the A → C transformation can be determined from Eq. (3), expressed in logarithm form as follows:

$$\ln\frac{\Delta T}{f(\alpha)} = \ln\frac{A}{\beta} - \frac{E}{RT} \tag{4}$$

The degree of conversion of aragonite to calcite, α, was calculated from curve *b* in Fig. 4, according to the approximation $\alpha \cong S/S_t$, where S is the peak area at

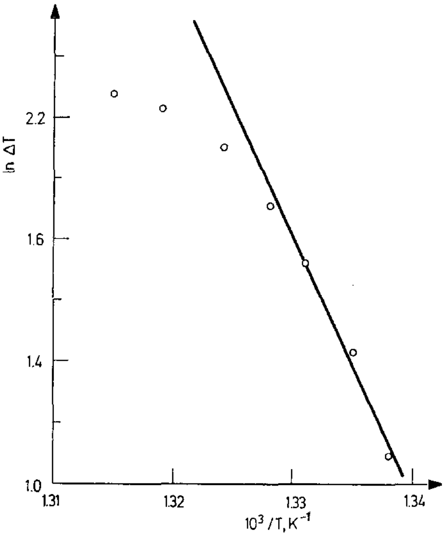

Fig. 7. Plot of ln ΔT *vs.* $1/T$. (The values of ΔT and T have been taken from curve *b* in Fig. 4; α range: $0.05 \leq \alpha \leq 0.7$.)

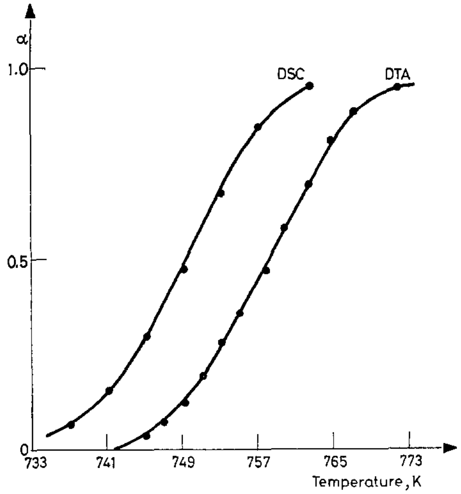

Fig. 8. α *vs.* T curves derived from the thermal curves in Fig. 4

temperature T and S_t is the total peak area. This approximation is supported by the data in Fig. 5, which show that a good correlation exists between sample weight and peak area. The α *vs.* T curve then obtained is shown in Fig. 8.

The plots of ln $\Delta T/(\alpha)$ *vs.* $1/T$ are included in Fig. 9, using the five mechanisms listed in Table 1. As shown in this Figure, poor correlations are obtained, and only for the unimolecular decay law (F_1) does the fitting of the data show a slightly better correlation (0.988); even so, the activation energy calculated from the slope (650 kJ/mole) is larger than that obtained from the isothermal experiments.

Therefore, although the kinetic analysis of the DTA curve is improved if the change in $\ln f(\alpha)$ with temperature is considered, marked discrepancies still exist between the isothermal and non-isothermal kinetic parameters. In our view, the reason is associated with the incorrect assumption of considering the height of the signal curve, ΔT, simply to be directly proportional to the reaction rate, as multiple variables affect a DTA curve [26].

On the other hand, we have carried out the kinetic analysis of the DTA curve following Dollimore *et al.*'s method [11], based on the calculation of $d\alpha/dT$ from the tangents to the α *vs.* T curve. The rate of the A → C transformation, $d\alpha/dT$, was deduced from the $\Delta\alpha/\Delta T$ ratio. The range of ΔT was 4°, the minimum value attained by the sensitivity of the experimental system used here.

According to Dollimore *et al.* [11], the rate law which applies in the A → C phase transition is an Avrami–Erofeev mechanism (A_4) for which $f(\alpha) = (1 - \alpha)[-\ln(1 - \alpha)]^{3/4}$. Thus, the DTA curve in Fig. 4 was analyzed with

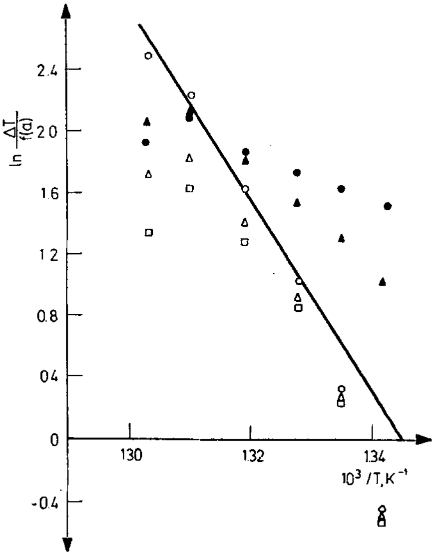

Fig. 9. Kinetic analysis of the DTA curve in Fig. 4 by kinetic laws listed in Table 1. (The assumption $\Delta T \propto d\alpha/dT$ has been used. α range: $0.08 \leq \alpha \leq 0.90$.) ○ F_1, ▲ A_2, ● A_3, □ R_2, △ R_3

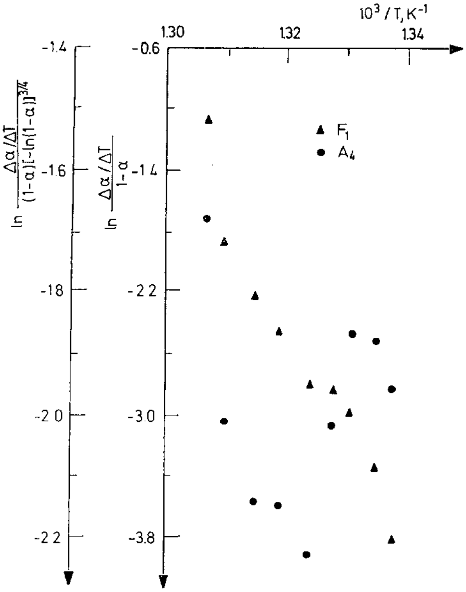

Fig. 10. Kinetic analysis of the DTA curve in Fig. 4 by different kinetic laws. (The assumption $d\alpha/dT \propto \Delta\alpha/\Delta T$ has been used. α range: $0.08 \leq \alpha \leq 0.80$.)

the help of Eq. (3), using the five $f(\alpha)$ functions included in Table 1, and extended to mechanism A_4. A few representative plots are shown in Fig. 10, where some of the mechanisms have been omitted for clearness.

According to these results, it is not possible to get a satisfactory fit of the data, because of the scattering of the points observed in Fig. 10, particularly for the Avrami–Erofeev mechanism. These calculations give rise to serious doubts as to the conclusions reported by Dollimore *et al.* [11] concerning the method of determining the mechanism of phase transitions from DTA curves. The limitation of the method is probably due to the inaccuracy of determining $d\alpha/dT$ as $\Delta\alpha/\Delta T$. Such a method of analyzing thermogravimetric traces was criticized elsewhere [27].

In the DSC technique, the value of the reaction rate is directly proportional to the DSC signal at any time during the reaction, and the extent of this, α, corresponds to the ratio of partial area to total area at each given temperature.

The fraction of aragonite transformed to calcite at different temperatures evaluated from the DSC curve in Fig. 4, is shown in Fig. 8. The results obtained by applying Eq. (3) to the kinetic data of the DSC curve are collected in Fig. 11. From the correlation coefficients of the mechanisms plotted in this Figure, the following conclusion is fairly evident. The data can only be moderately well fitted to unimolecular decay law kinetics, with a correlation coefficient of 0.997. The activation energy calculated from the slope of the plot for this mechanism gives a value of 575 ± 30 kJ/mole, in good agreement with that obtained from

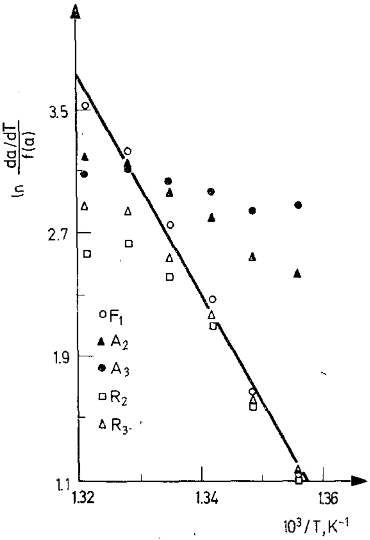

Fig. 11. Kinetic analysis of the DSC curve in Fig. 4 by the kinetic laws listed in Table 1. (α range: $0.07 \leq \alpha \leq 0.85$.) ○ F_1, ▲ A_2, ● A_3, □ R_2, ▲ R_3

the isothermal kinetic data. These results further support the above statement that the A → C phase transformation follows the unimolecular decay law. On the other hand, the high activation energy obtained is consistent with a substantial rearrangement of the structure, as the A → C phase transformation is an irreversible, reconstructive transformation changing the coordination number of the Ca(II) ions from 9 to 6.

Conclusions

Two conclusions can be drawn from the results decribed. First of all, the possibility of obtaining kinetic parameters of phase transitions and crystallization processes from DTA curves should be considered carefully, owing to the difficulty of determining accurately the reaction rate of the process. Thus, the most commonly used method, the Piloyan method, leads to a poor fitting of the kinetic data and important discrepancies are found between the evaluated activation energy and that calculated from the isothermal kinetic data.

Secondly, in differential scanning calorimetry, where the reaction rate is proportional to the height of the peak from the base-line, it is possible to obtain a good fitting of the data. The kinetic results obtained with this technique, at least when a phase transition is concerned, are in good agreement with the isothermal results.

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Zusammenfassung — Die Differentialthermoanalyse und DSC wurden zur Untersuchung der Kinetik von Phasenübergängen eingesetzt. Die Umwandlung Aragonit/Calcit wurde als Testreaktion gewählt.

Bedeutende Diskrepanzen wurden zwischen den kinetischen Ergebnissen der DTA und den durch isotherme kinetische Messungen erhaltenen Ergebnissen beobachtet. Diese Abweichungen sind damit verbunden, daß es schwierig ist, die Reaktionsgeschwindigkeit des Vorgangs aus einer DTA-Kurve genau zu ermitteln.

Bei DSC-Messungen,wo die Reaktionsgeschwindigkeit durch die Höhe des Peaks von der Grundlinie gegeben ist, kann eine befriedigende Anpassung der Daten erhalten werden, und die durch diese Technik erhaltenen kinetischen Ergebnisse sind in guter Übereinstimmung mit den isothermen Ergebnissen.

Резюме — Для изучения кинетики фазовых переходов были использованы дифференциальный термический анализ и дифференциальная сканирующая калориметрия. В качестве испытательной реакции было взято фазовое превращение арагонит/кальцит. Заметные различия наблюдались между кинетическими результатами, полученными на основе ДТА и изотермических измерений. Такое разногласие обусловлено трудностью точного определения константы скорости процесса превращения из ДТА-кривых. Наоборот, при ДСК измерениях, где скорость реакции определяется высотой пика от базисной линии, представляется возможным получить удовлетворительное совпадение данных и в связи с чем кинетические результаты, полученные этим методом, хорошо согласуются с изотермическими данными.