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A STUDY OF THE KINETICS OF THE PHASE TRANSITION ARAGONITE → CALCITE BY DILATOMETRIC THERMAL ANALYSIS

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The first-order phase transition in the system aragonite-calcite ($CaCO_3$) was studied with natural and synthetic aragonites. The studies were carried out by dilatometry on a derivatograph, under non-isothermal conditions. It was found that the polymorphic transformation of aragonites into calcite is described by the Avrami equation $l = 1 - \exp(-kt^n)$, with the exponent n having a value close to 1. The activation energy values found for the aragonites studied were 184—205 kJ/mol, while the values of the pre-exponential factor z were 10^{14}—10^{12} s^{-1} in the conversion range $l = 0.10 - 0.66$.

The solid-state reaction studied was the transformation of the rhombic $CaCO_3$ modification aragonite into the trigonal modification calcite. The transformation is of the $A_s \rightarrow B_s$ type and is accompanied not only by the absorption of heat, but also by an increase in the volume of the initial sample. Since the transformation of aragonite into calcite is proportional to the measured linear dilatation, formal kinetic parameters characterizing the process can be calculated by means of the plot dilatation of the sample *vs.* temperature [1].

The kinetics of such first-order solid-state transitions are usually studied under isothermal conditions [2–4]. By using a derivatograph with a dilatometric attachment, one can carry out the investigation under a steady rise of temperature [5, 6]. With this technique, the phase transition is recorded in the form of two thermoanalytical curves; the dilatometric curve TD and the derivative dilatometric curve DTD, instead of the usual TG and DTG curves (Fig. 1).

To determine the kinetic parameters of the phase transition of aragonite into calcite from the thermoanalytical curves TD and DTD, calculation methods of formal kinetics based on the conversion were applied, analogously at for thermoanalytical curves associated with weight change, that is TG and DTG curves [7, 10].

In the general form, the rate of the phase transition $\frac{dl}{dt} = k \cdot f(l)$ and the temperature-dependence of the rate constant $k = z \cdot \exp\left(-\frac{E}{RT}\right)$ for non-isothermal conditions can be expressed in the following form:

$$\frac{\mathrm{d}l}{f(l)} = \frac{z}{q} \exp\left(-\frac{E}{RT}\right) \mathrm{d}T \tag{1}$$

where l is the conversion of aragonite in the phase transition. l can also be expressed as $l = \frac{L_\mathrm{T}}{L_\infty}$, L_∞ being the final elongation of the sample after the transformation, in mm, and L_T the elongation measured in the experiment at the temperature T in mm.

The further symbols in Eq. (1) denote the following: q is the heating rate (degree/s), z the pre-exponential factor (s^{-1}), E the activation energy (kJ/mol), R the universal gas constant = 1.986 cal $\cdot$ $\mathrm{mol}^{-1}\mathrm{K}^{-1}$, T the temperature (K), and $f(l)$ the rate relationship of the formation and growth of the new phase, calcite, at the expense of the initial phase, aragonite.

By integration of Eq. (1) and subsequent taking of logarithms, it is transformed into the following form [7]:

$$\log g(l) - \log p(x) = B \tag{2}$$

where

$$g(l) = \int_0^1 \frac{\mathrm{d}l}{f(l)}, \quad B = \log \frac{zE}{Rq} = \text{const.}$$

and $p(x) = e^{\frac{-x}{x}} - \int_0^1 \frac{e^{-u}}{u}\,\mathrm{d}u$ (a tabulated function [8, 9]).

According to Šatava [7], within a narrow temperature interval the plot $\log g(l)$ *vs.* $\frac{1}{T}$ will be linear only for a correctly selected value of $f(l)$, analogously to $f(\alpha)$ in the case of TG and DTG curves, the theoretical expressions for which are listed in the Table of Ref. [7]. Hence, the task is reduced to finding the formal kinetic equation that will best describe the dilatometric curve obtained experimentally by the plot $\log g(l)$ *vs.* $\frac{1}{T}$. With the use of the value of $f(l)$ found in this manner and the value of $\frac{\mathrm{d}l}{\mathrm{d}T}$ from the DTD curve, Eq. (1) can be written in the linear form:

$$\ln\left[\frac{1}{f(l)} \cdot \frac{\mathrm{d}l}{\mathrm{d}T}\right] = \ln \frac{z}{q} - \frac{E}{RT}. \tag{3}$$

The activation energy can then be calculated from the slope of this straight line, and the pre-exponential factor z from the intercept with the ordinate.

Experimental

Natural and synthetic aragonites were chosen for the investigation. In the natural aragonite spectral analysis demonstrated a total of 0.06% impurities (Sr, Pb, Mg, Si). The synthetic aragonite was prepared, as suggested by Dana and Dana [11], by mixing boiling solutions (0.05 mol/l) of $CaCl_2$ and Na_2CO_3. X-ray diffraction analysis of the synthetic aragonite obtained showed the presence of pure aragonite with an insignificant amount of calcite.

The aragonites were ground to a particle size of 60 μm, and hollow cylindric samples (length ~3 cm, external diameter 1.7 cm, internal diameter 0.8 cm) were moulded using a pressure of 3000 bar. The samples were heated in air in the temperature range 320 to 420°, at a heating rate of 4°/min, in the derivatograph.

Discussion

A typical dilatogram showing the phase transformation of synthetic aragonite into calcite is shown in Fig. 1. The experimental values of l *vs.* $1/T$, measured for every 10° of temperature rise, were substituted into each of the kinetic equations listed in the Table presented in Ref. 7, i.e.

$$F_1 - \ln(1 - l) = kt$$

$$A_2 - \ln(1 - l)^{1/2} = kt$$

$$A_3 - \ln(1 - l)^{1/3} = kt\,.$$

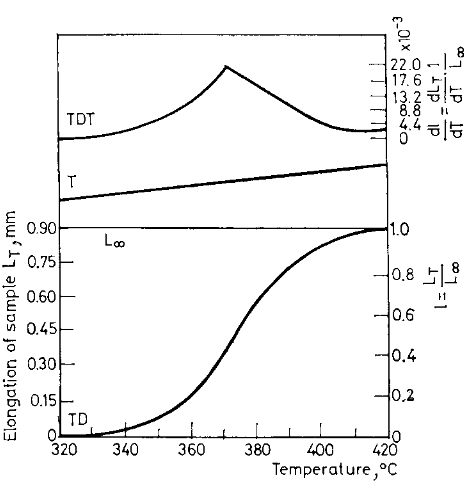

Fig. 1. Dilatometric curves for synthetic aragonite

It may be seen from Fig. 2 that within the conversion range $l = 0.66 - 0.10$, the relationship $\log g(l)$ *vs.* $\frac{1}{T}$ yields a straight line when the Avrami equation (A_2) and the first-order equation F_1 are used, that is $f(l) = (1 - l)\,[-\ln(1 - l)]^{1-1/n}$, or in the general form, $l = 1 - \exp(-kt^n)$, where the exponent n is defined by the order of the process in which the new phase is formed and grows. In our case, n can assume the values 1 and 2. Of these two mechanisms, only one can be true. The kinetic parameters following from Eqs F_1 and A_2, calculated by means of Eq. (3) (Fig. 3), yielded the following values, respectively:

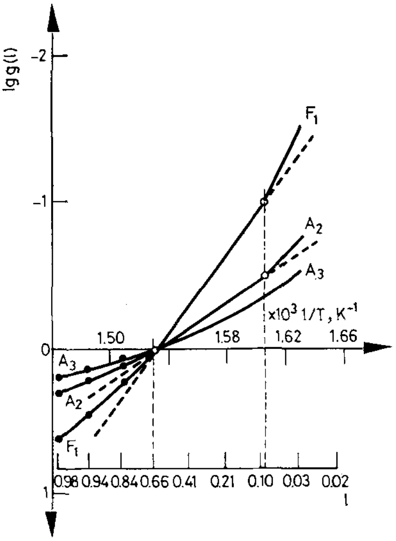

Fig. 2. Graphical determination of the kinetic equation describing the dilatometric curves of the transition of aragonite into calcite (after Šatava)

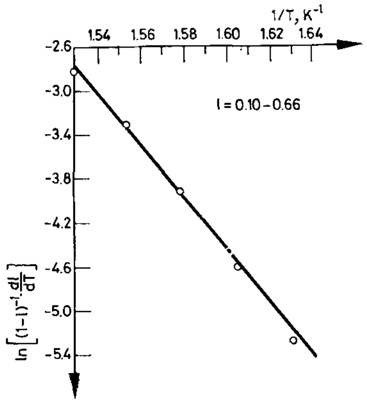

Fig. 3. Determination of the activation energy for the phase transition of synthetic aragonite into calcite

$$E = 205 \text{ kJ/mol} \qquad Z = 1.6 \cdot 10^{14}\,\text{s}^{-1} \qquad (F_1)$$

$$E = 92 \text{ kJ/mol} \qquad Z = 2 \cdot 10^{5}\,\text{s}^{-1}. \qquad (A_2)$$

According to theoretical concepts for solids, the pre-exponential factor z, in our case, should have a value of the order of $10^{14} - 10^{12}$. Considering the value z as the second criterion of the satisfactoriness of the model applied to describe the transition observed, and comparing the values obtained with the results of other researchers [2 – 4], one may conclude that the phase transition of aragonite into calcite, within the range $l = 0.10$ to 0.66, is described by the particular case of the Avrami equation when $n = 1$.

Table 1

Kinetic parameters of the transformation of aragonites into calcite

Aragonite	Temperature range of transformation, °C	Temperature of maximum transformation rate, °C	E, kJ mol	z, s^{-1}	Conversion l	Values of E in the literature*
Synthetic	330–420	371	205	$1.6 \cdot 10^{14}$	0.10–0.66	209 [4]
Natural	330–420	364	184	$4.7 \cdot 10^{12}$	0.16–0.65	184 [4]

* Literature values originally in kcal/mol: 50 and 44 rsp.

The kinetic parameters characterizing the phase transition of aragonites into calcite are listed in Table 1. The small differences between the values of the kinetic parameters for the different aragonites are presumably connected with particular individual features of the starting materials.

The satisfactory agreement of the kinetic parameters calculated from the non-isothermal dilatometric curves with isothermal constants cited in the literature [4] and with theoretical calculations [13] allow the conclusion that first-order phase transitions can successfully be studied under non-isothermal conditions by using dilatometric data recorded with a derivatograph.

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Résumé — On a étudié la transition de phases du premier ordre qui a lieu dans le système aragonite-calcite ($CaCO_3$) dans des aragonites minérales, naturelles et synthétiques. Les études ont été effectuées par dilatométrie dans un dérivatographe en conditions non-isothermes. On a trouvé que la transformation polymorphe des aragonites en calcite est décrite par l'équation d'Avrami $l = - \exp(-kt^n)$, l'exposant n étant proche de 1. Les valeurs des énergies d'activation trouvées pour les aragonites étudiées se sont élevées à 185 . . . 207 kJ/mole, les valeurs du facteur pré-exponentiel z à $10^{14} \ldots 10^{12}$ s^{-1}, dans l'intervalle de conversion $l =$ $= 0.10 \ldots 0.66$.

ZUSAMMENFASSUNG — Der Phasenübergang erster Ordnung wurde im System Aragonit-Kalzit ($CaCO_3$) an natürlichen und synthetischen anorganischen Aragoniten untersucht. Die Untersuchungen wurden durch Dilatometrie in einem Derivatographen unter nicht-isothermen Bedingungen durchgeführt. Es wurde festgestellt, daß die polymorphe Umwandlung der Aragonite zu Kalziten durch die Avrami-Gleichung $l = 1 - \exp(-kt^n)$ beschrieben wird, wobei der Exponent n einen Wert in der Nähe von 1 hat. Die für die untersuchten Aragonite gefundenen Werte der Aktivierungsenergie waren 185 . . . 207 kJ/Mol, die Werte des präexponentiellen Faktors z betrugen $10^{14} \ldots 10^{12}$ s^{-1} im Konversionsbereich $l = 0.10 \ldots 0.66$.

Резюме — Изучался фазовый переход перевого рода на системе арагонит-кальцит ($CaCO_3$). Объектом изучения являлись неорганические арагониты: природные и искусственные. Исследования проводились дилатометрическим методом на дериватографе в неизотермическом режиме. Найдено, что полиморфное превращение арагонитов в кальцит удовлетворительно описывается уравнением Аврами $l = 1\text{-}\exp(-kt^n)$, где n — имеет значение, близкое к единице. Для исследуемых арагонитов найденные значения энергии активации составляют 184—205 кдж/моль, а значения предэкспоненциальных множителей = 10^{14}—10^{12} сек$^{-1}$ для степени превращения $l = 0.10$—0.66.